

Stabilization of Gamma-Irradiated Poly(vinyl Chloride) by Epoxy Compounds. I. Radiation Yield of Hydrogen Chloride and Changes of Epoxy Group Concentration in Gamma-Irradiated PVC–Stabilizer Mixtures

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Synopsis

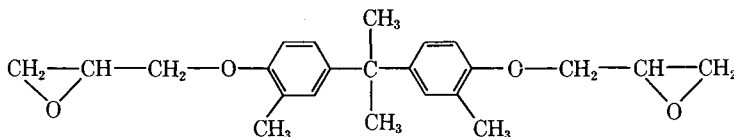
The G_{HCl} values of γ -irradiated PVC mixtures and the changes of the epoxy group concentration were studied after addition of various amounts of five epoxy stabilizers: diglycidyl ether of 2,2-bis(4-hydroxy-3-methyl phenyl)propane (I), diglycidyl ether of 2,2-bis(4-hydroxy-3-nitrophenyl)propane (II), styrene oxide (1,2-epoxy ethyl benzene) (IV), epoxidized ricinus oil (VI), and epoxidized soybean oil (Drapex 6.8.) (VII). It is stated that only about 50% of epoxy groups, declining in the system, take part in binding of HCl; the rest of these groups disappear as a consequence of other reactions. In connection with the data of the previous paper,¹ the results presented indicate that the process of stabilization goes in two stages. In the first stage the process consists of the HCl capture by the epoxy groups; in the second stage, due to the remaining part of the stabilizer molecule, a protective effect occurs. This effect consists, for the stabilizers I, II, IV, of gaining the energy by the benzene ring and, for the stabilizers VI, VII, of a mechanical drawing of polymer chains, which makes the energy transfer more difficult. Having the greatest content of epoxy oxygen (about 10%), the styrene oxide (IV) stabilizes best.

INTRODUCTION

In our previous paper¹ we have investigated changes of hydrogen chloride radiation yield in gamma-irradiated mixtures of PVC with three epoxy stabilizers, in a nitrogen atmosphere. Now we present three consecutive works on the radiation stabilization of PVC with epoxy compounds. This cycle discloses the four further epoxy stabilizers and consists of investigations on: HCl radiation yield in nitrogen and oxygen atmosphere and epoxy group concentration changes (Paper I), oxidation process of PVC depending on stabilizer content (Paper II), and changes of the nature and the degree of unsaturation in PVC–stabilizer mixtures (Paper III).

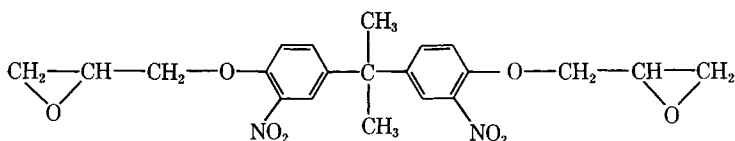
First of all, for the sake of clarity, we will enumerate all epoxy compounds which were used as stabilizers in all our investigations. The compounds are distinguished into two groups: the stabilizers with aromatic ring (I, II, III, IV) and the linear stabilizers (V, VI, VII).

I. Diglycidyl ether of 2,2-bis(4-hydroxy-3-methyl phenyl)propane, oxirane



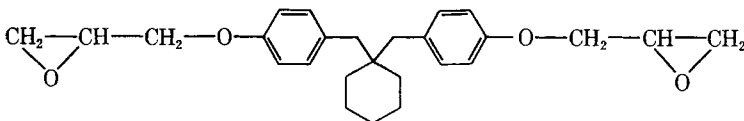
group content: calcd 8.68%; determined, 6.30%

II. Diglycidyl ether of 2,2-bis(4-hydroxy-3-nitrophenyl)propane, oxirane group



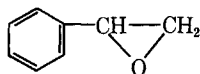
content: calcd 7.43%; determined 4.09%

III. Diglycidyl ether of 1,1-bis(4-hydroxyphenyl)cyclohexane, oxirane group

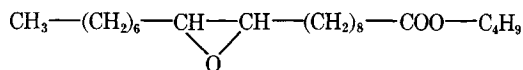


content: calcd 8.41%; determined 7.54%

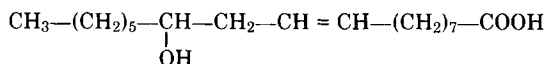
IV. Styrene oxide (1,2-epoxy-ethyl-benzene), oxirane group content: calcd



13.33%; determined 9.54%

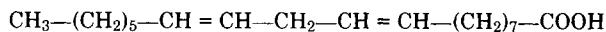
V. Butyl-*cis*-9,10-epoxystearate

oxirane group content: calcd 4.52%; determined 1.25%

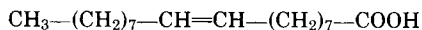
VI. Epoxidized ricinus oil contains 80% of ricinoleic acid (12-hydroxy-*cis*-9-octadecenoic acid)

oxirane group content: determined 2.08%

VII. Epoxidized soybean oil, plasticizer produced by Argus Chemical, N.Y.—Drapex 6.8, contains 53% of linoleic acid



and 34% of oleic acid



oxirane group content: producer's data 6.2%; determined 5.9%

In our former paper we investigated the gamma-irradiated mixtures of PVC with stabilizers I, III, V in a nitrogen atmosphere only, and we have presented the total radiation yield for a given dose G_{HCl} (number of molecules of HCl evolved from PVC as a result of dehydrochlorination, computed for 100 eV of absorbed energy), momentary radiation yield $G_{\text{HCl}}^{\Delta t}$, and initial radiation yield G_{HCl}^i vs. dose and admixture of the stabilizer.

In this work (Paper I) we present the changes of G_{HCl} , $G_{\text{HCl}}^{\Delta t}$, and G_{HCl}^i in the mixtures of PVC with stabilizers II, IV, VI, VII, gamma-irradiated in a nitrogen

atmosphere, and in the mixtures of PVC with the stabilizers I, IV, VI, VII, gamma-irradiated in an oxygen atmosphere.

We present also in Paper I the changes of the epoxy groups concentration in selected systems. From the stabilizers with the aromatic ring, the stabilizers I and IV were chosen, while from the group of linear stabilizers the stabilizer VI was chosen. The investigations were performed both in a nitrogen and oxygen atmosphere.

EXPERIMENTAL

Both the preparation of samples and the measurements of the kinetics of the dehydrochlorination were the same as in our former works.^{1,2} The oxirane group content in epoxy compounds I–VII was determined by the titration with the solution of hydrochloric acid in dioxane.³ The samples were irradiated, as formerly, in a RHM- γ -20 irradiation unit. Dose rate, determined by a Fricke dosimeter, is given in each figure. The irradiation in both inert and oxygen atmosphere was carried in the same manner. The gas flux was 50 cm³/min.

The content of the epoxy groups in PVC–stabilizer mixtures was determined by a colorimetric method,⁴ on the basis of the reaction with 2,4-dinitrobenzene sulfon acid in dioxane. The ester formed enters into color reaction with the solution of piperazine hydrate in dimethyl formamide. The absorption was measured at a wavelength of 390 nm.

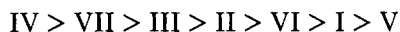
When, as a consequence of radiolysis, the PVC samples were colored, a blank test was performed, where, in place of 2,4-dinitrobenzene sulfon acid, dioxane was added. The absorption of this test was subtracted from the absorption of the sample. The content of the epoxy groups is done from the analytical curve standardized for a correspondent pure epoxy compound.

RESULTS AND DISCUSSION

The results of measurements of the total radiation yield G_{HCl} vs. dose, drawn for each epoxy compound, represent similar curves both in a nitrogen and oxygen atmosphere. Then we give only one set of curves (Fig. 1) for the stabilizer IV as an example. Our conclusions are based on quantitative comparison of similar curves for another stabilizers.

In connection with the data of our previous work¹ concerning stabilizers I, III, V, the results of measurements of the G_{HCl} vs. dose, for PVC mixtures containing various amounts of stabilizers II, IV, VI, VII, characterize the totality of the process of stabilization in inert atmosphere, from the beginning of irradiation to a moment of absorption of the total dose of gamma-rays. It permits us to order all of the used stabilizers according to descending stabilization effect, for the selected contributions of stabilizer admixture [mol oxirane groups/mole PVC monomer units (mu)] and for the selected, arbitrarily chosen, doses (Mrad = 10⁴ Gy = 10 kGy).

For a small stabilizer admixture from 0.24×10^{-3} to 1.87×10^{-3} mol epoxy group/mole PVC mu (stoichiometric 0.89 – 2.62×10^{-3} mol) we have for the dose 20 kGy



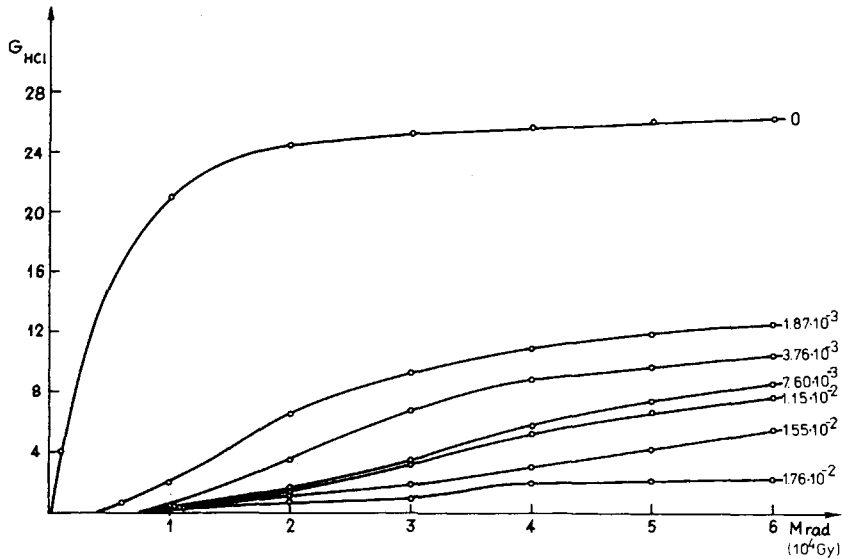


Fig. 1. G_{HCl} vs. γ -irradiation dose for PVC with an admixture of stabilizer IV (mol oxirane groups/mol PVC μ) in a nitrogen atmosphere. Dose rate: $8.78 \times 10^{17} \text{ eV}\cdot\text{cm}^{-3}\cdot\text{min}^{-1}$.

and for the dose 60 kGy

$$\text{IV} > \text{VII} > \text{III} > \text{II} > \text{V} > \text{I} > \text{VI}$$

For the admixtures higher by one order: from 0.23×10^{-2} to 1.76×10^{-2} mol epoxy groups/mole PVC μ (stoichiometric $0.83\text{--}2.45 \times 10^{-2}$ mol) we have for

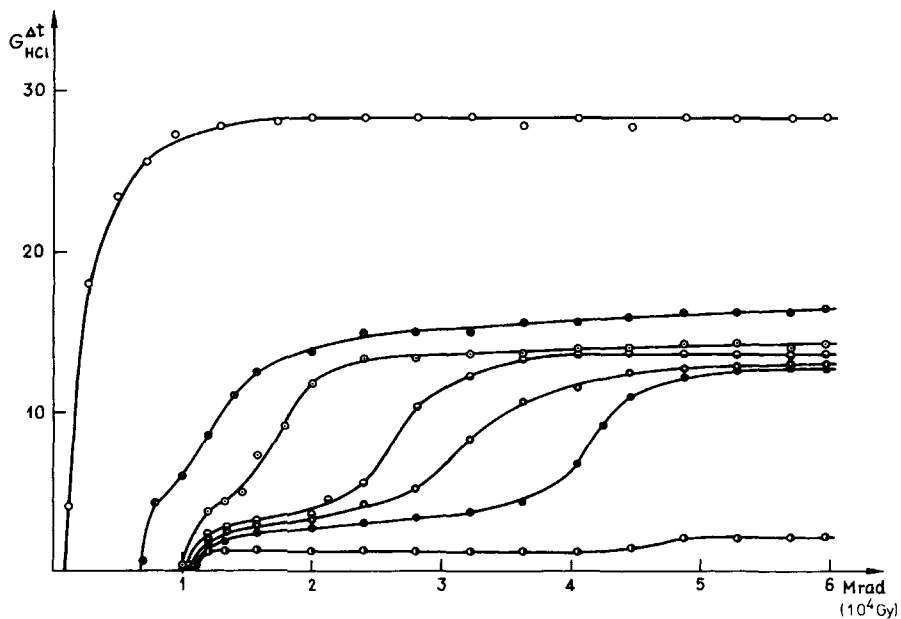


Fig. 2. $G_{\text{HCl}}^{\text{At}}$ vs. γ -irradiation dose for PVC with an admixture of stabilizer IV (mol oxirane groups/mol PVC μ), in a nitrogen atmosphere: (○) 0; (⊗) 1.87×10^{-3} ; (⊙) 3.76×10^{-3} ; (⊖) 0.76×10^{-2} ; (○) 1.15×10^{-2} ; (●) 1.55×10^{-2} ; (●) 1.76×10^{-2} . Dose rate: $8.78 \times 10^{17} \text{ eV}\cdot\text{cm}^{-3}\cdot\text{min}^{-1}$.

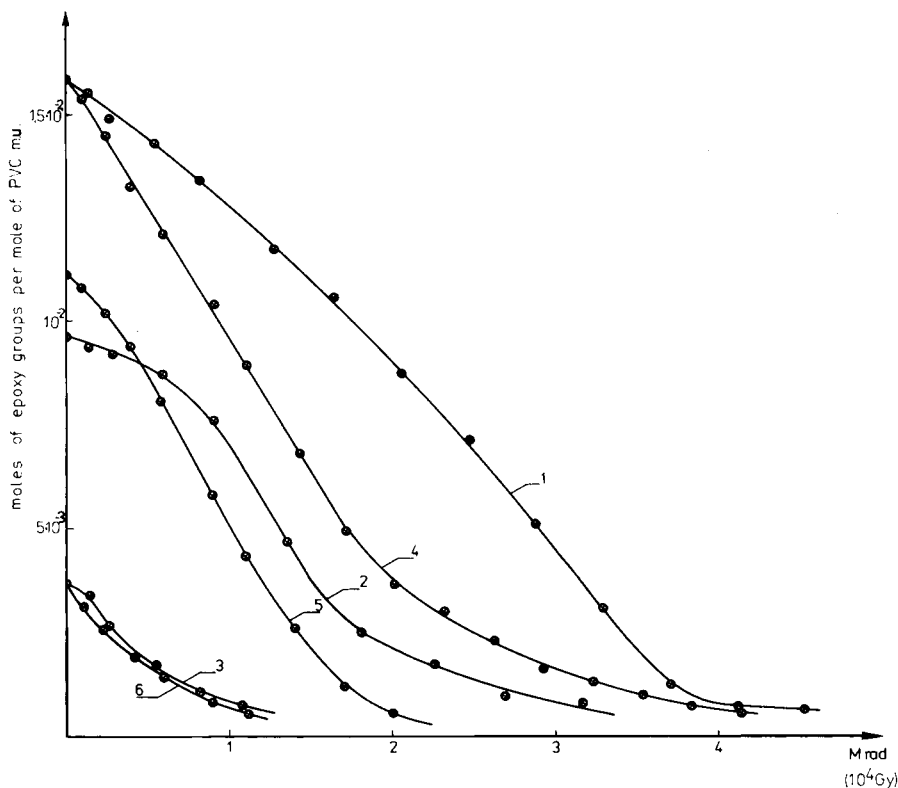


Fig. 3. The changes of concentration of epoxy groups (mol/mol PVC mu) vs. γ -irradiation dose; designations 1, 2, and 3 refer to stabilizers IV (1.55×10^{-2}), I (1.16×10^{-2}), and VI (3.82×10^{-3}), respectively, in N_2 atmosphere; designations 4, 5, and 6 refer to stabilizers IV (1.76×10^{-2}), I (1.16×10^{-2}), and VI (3.82×10^{-3}), respectively, in O_2 atmosphere.

the dose 20 kGy



and for the dose 60 kGy



The results of measurements of G_{HCl} in an oxygen atmosphere for the stabilizers I, IV, VI, VII permit us to order these stabilizers as follows: $IV > VII > I > VI$. Neither the change of stabilizer admixture ranging from 0.41×10^{-3} to 1.76×10^{-2} mol epoxy group/mole PVC mu nor the variation of the dose from 20 to 50 kGy do not affect this sequence.

From the above observations the following two conclusions can be drawn: (a) The styrene oxide stabilizes best and includes the greatest content of the oxirane oxygen (stoichiometric 13.3%); (b) the effect of stabilization is evidently not dependent on such fundamental difference in the structure of the stabilizer as a presence or not of the aromatic ring.

An example of the momentary radiation yield G_{HCl}^{Δ} vs. dose, in nitrogen atmosphere, is presented in Figure 2 for stabilizer IV. Similar curves we obtained for the oxygen atmosphere.

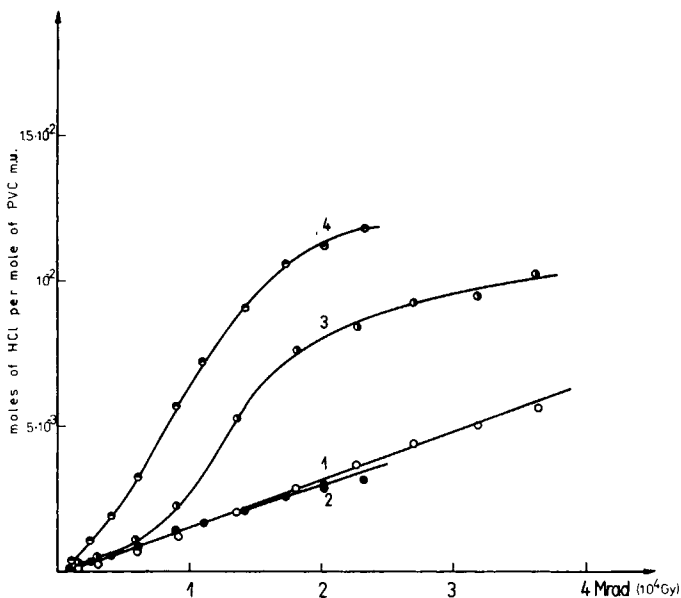


Fig. 4. The amounts of HCl bound by epoxy groups of stabilizer I (mol HCl/mol PVC mu) vs. γ -irradiation dose; designations 1, 3 refer to N_2 atmosphere and 2, 4 to O_2 atmosphere, 1, 2 determined and 3, 4 computed stoichiometrically.

The form of kinetic curves indicates that process of stabilization runs in two stages, in agreement with the character of the radiolysis of the pure PVC. In the first stage a marked influence of epoxy group on the decrease of G_{HCl}^{Δ} value

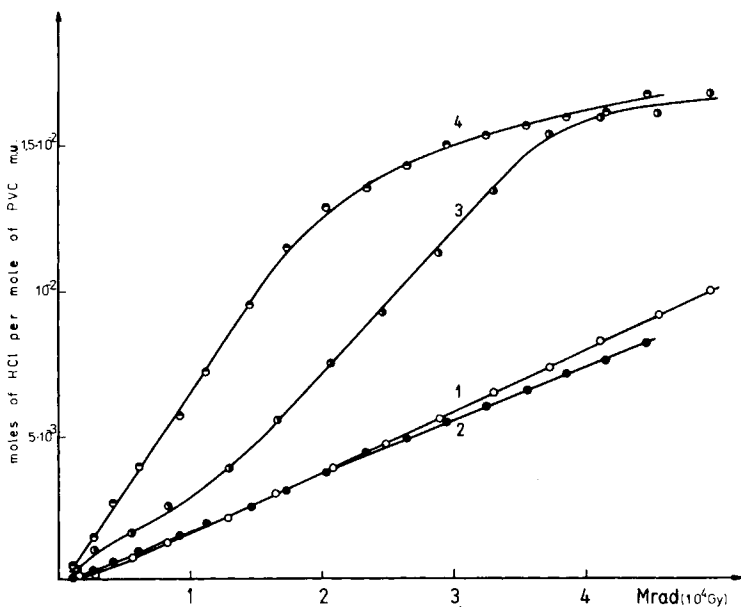


Fig. 5. The amounts of HCl bound by epoxy groups of stabilizer IV (mol HCl/mol PVC mu) vs. γ -irradiation dose; designations 1, 3 refer to N_2 atmosphere and 2, 4 to O_2 atmosphere, 1, 2 determined and 3, 4 computed stoichiometrically.

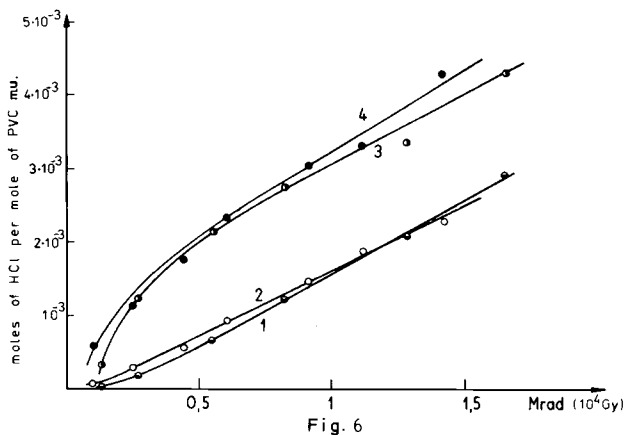


Fig. 6. The amounts of HCl bound by epoxy groups of stabilizer VI (mol HCl/mol PVC mu) vs. γ -irradiation dose; designations 1, 3 refer to N_2 atmosphere and 2, 4 to O_2 atmosphere, 1, 2 determined and 3, 4 computed stoichiometrically.

is evident. In this stage the process consists of HCl capture by the epoxy groups with a simultaneous protective effect of stabilizer with respect to polymer. In the second stage the structural elements of the stabilizer's molecule other than epoxy groups affect the radiation yield of HCl. The mechanism of protective effect in the second stage depends, for the stabilizers I–IV, on gaining the energy by the aromatic ring, and, for linear stabilizers V–VII, it depends upon their plasticizing properties. The plasticizers cause a mechanical drawing of polymer chains, which makes the energy transfer more difficult.

The changes of the concentration of the epoxy groups vs. dose, presented in Figure 3, explains two-stage mechanism of the stabilization process. For the doses at which in the first stage of stabilization an increase of the momentary radiation yield G_{HCl}^A appears, nearly total decay of epoxy oxygen takes place.

The apparent differences in the rates of the decay of the epoxy groups for individual stabilizers in Figure 3 do not possess an unambiguous explanation. In the case of the stabilizer VI the short time decay of the epoxy groups can illustrate their very small initial concentration. In the case of stabilizer I and IV, however, the concentration of the epoxy oxygen may explain only partially the differences in forms of obtained curves. The main reason of various rates of the decay of the epoxy groups is, in our opinion, the quite different character of the substituents at the carbon atom of the epoxy ring. This character has a fundamental influence on the contribution of the ion structure in both mesomeric forms, i.e., on the reactivity.

The rate of the decay of the epoxy groups is considerably greater in an oxygen atmosphere. The system with the styrene oxide (IV) is most affected by the presence of the oxygen. In the case of the linear stabilizer (VI) the influence of the oxygen atmosphere is insignificant.

We have investigated the correlation between the changes of the epoxy group concentration and the quantity of HCl bound by a stabilizer. The amounts of the bound HCl (mol HCl/mol PVC mu) vs. dose, both in a nitrogen and oxygen atmosphere, are presented in Figures 4–6. For comparison, on the base of the

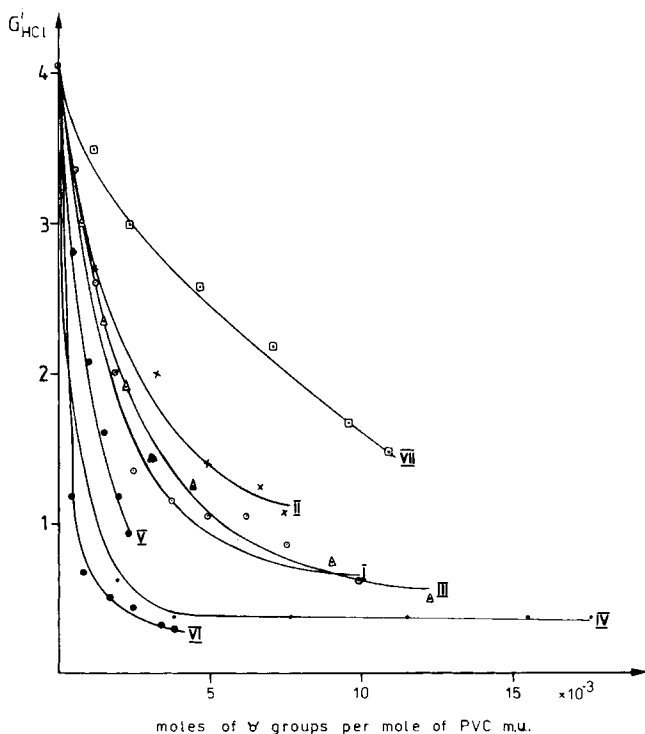


Fig. 7. G_{HCl}^i vs. stabilizer admixture in moles of oxirane groups per mole of PVC monomer units (μ) in N_2 atmosphere. Stabilizer: I (\circ); II (\times); III (Δ); IV (\cdot); V (\bullet); VI (\bullet); VII (\square).

loss of epoxy groups, we have calculated the quantity of HCl, which should be bound stoichiometrically.

The difference between the determined amount of HCl bound by epoxy groups and the stoichiometric amount is very large. The presence of the oxygen increases this difference, and it is greater for the stabilizers I and IV (Figs. 4 and 5) than for the linear stabilizer (Fig. 6). Less than 50% of epoxy groups declining in the system takes part in binding of HCl (for stabilizer VI somewhat more than 50%). This fact proves that the action of the epoxy groups is not entirely limited to a binding of HCl liberated in PVC radiolysis. We will consider this problem in Paper III of the cycle, where the degree of unsaturation in the systems investigated will be examined.

As can be seen in Figures 4-6, the atmosphere of the oxygen has no influence on the amount of HCl bound by stabilizer, although it has an evident bearing on the rate of the decay of the epoxy groups (Fig. 3). These data, when compared with HCl radiation yields, permit us also to state that the efficiency of the addition of HCl to the epoxy ring does not depend on the amount of the evolved HCl. The radiation yield of HCl is greater in the oxygen while the amounts bound by stabilizer are the same in the both atmospheres.

The presented results confirm the well-known fact that epoxy compounds are acceptors of the hydrogen chloride.⁵ In connection with this fact the dehydrochlorination rate may be changed because of autocatalytic effect of HCl. In our case this last process seems to be less significant, since the irradiation of samples

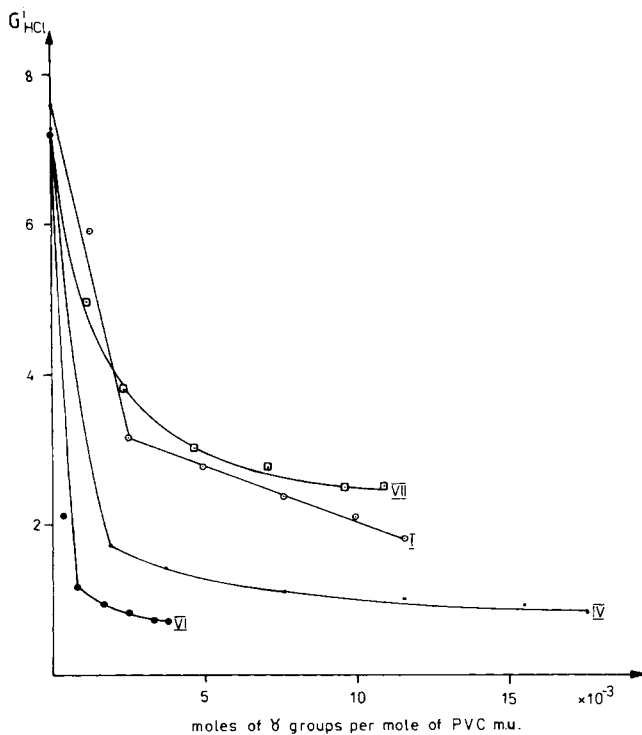


Fig. 8. G_{HCl}^i vs. stabilizer admixture in moles of oxirane groups per mole of PVC monomer units (μ) in O_2 atmosphere. Stabilizer: I (○); IV (·); VI (●); VII (◻).

takes place with a simultaneous washing of the material by a flux of dry gas and the HCl is removed continuously from the polymer.

However, the limitation to the above conclusion only (i.e., epoxy compounds = acceptors of HCl), on the basis of the investigations of the decay of epoxy groups, as is done by the majority of authors, seems to be a mistake. As it followed from our results, about half of the epoxy oxygen disappears from the system as a consequence of reactions other than the reaction of addition of HCl. There is a possibility that reactions with double bonds take place⁶; there are also possible reactions of the creation of ether linkage.⁷

The dependence of the initial radiation yield G_{HCl}^i on the stabilizer content confirms this general picture of the stabilization process. The G_{HCl}^i values vs. stabilizer admixture are presented in Figure 7 for all stabilizers used in a nitrogen atmosphere, as well as in Figure 8 for stabilizers I, IV, VI, and VII in oxygen.

The stabilizer admixture results in elongation of the induction period. The G_{HCl}^i value is most affected by the stabilizers IV and VI. However, none of the basic elements of the structure of stabilizer has more distinct influence on the decrease of G_{HCl}^i value. Certainly the oxirane group is not only factor affecting this value. For instance, the stabilizer VII with 5.9% of epoxy oxygen diminishes the G_{HCl}^i value to 1.45 whereas stabilizer VI with 2.1% of epoxy oxygen to 0.33, which represents only 8% of the initial yield in pure PVC. Both of these stabilizers, being glycerides of fatty acids, have very similar structure, which amounts

TABLE I
Percentage Decrease of G_{HCl} Values in γ -Irradiated PVC-Stabilizer Mixtures

Stabilizer	Atmosphere	Content of stabilizer (%)					
		2 Mrad (20 kGy)		5 Mrad (50 kGy)		6 Mrad (60 kGy)	
		0.5	4.5	0.5	4.5	0.5	4.5
I	N ₂	19	92			9	68
	O ₂	14	73	7	46		
II	N ₂	27	65			18	43
III	N ₂	28	93 ^a			18	68 ^a
IV	N ₂	73	97			52	65
	O ₂	65	93	44	88		
V	N ₂	16	85			13	66
VI	N ₂	25	91			6	57
	O ₂	12	73	5	44		
VII	N ₂	38	70			34	67
	O ₂	31	74	25	64		

^a 4% of the stabilizer.

to simple chains of fatty acids with 18 carbon atoms and one or two double bonds. Therefore, slight differences in the molecular structure decide in this case about the mechanism of stabilization.

Another example of differences of this mechanism represents the stabilizer II, which is the least effective among all of the diglycidyl ethers. The stabilizer II differs from the remaining ethers, by the presence of NO₂ group in benzene ring. The NO₂ group is particularly electrophilic, namely, it perturbs to a high degree the π -electrons system of the ring, thereby reducing the ability of the ring to the resonant dissipation of the energy. The NO₂ group is also an effective scavenger of electrons produced in the process of radiolysis. In the macromolecules of PVC a great number of chlorine atoms, which are also electron scavengers, is present. In this situation the competitive reactions of electron scavenging by NO₂ group and chlorine atoms appear. A small effect of stabilization observed in this case we explain as a superposition of the perturbation process of the π -electrons system and of the transfer of electrons, captured by NO₂ group, to the polymer. This explanation may illustrate the lack of advantageous effect of stabilization in spite of the high reactivity of the NO₂ group.

The diminution of the G_{HCl} value in relation to the pure PVC is greater in oxygen than it is in an inert atmosphere. This fact, however, is not the evidence for the antioxidative action of all used stabilizers (I, IV, VI, VII). In Paper II we shall demonstrate that, in the studied systems, the stabilizers VI and VII have no antioxidative properties.

The collected data of effectiveness of the stabilizers, used evaluated as the percentage decrease of G_{HCl} value, are presented in Table I. On account of the practical importance of these results, the content of stabilizer is given, in Table I in wt %.

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