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Photooxidation of Poly(vinyl Chloride). I. Influence of Film Thickness and Temperature on the Kinetics of Formation of CO Groups

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ABSTRACT

The photooxidation of PVC was followed by IR titration of $>C=O$ groups. The kinetics of formation of these groups is characterized by an initial autocatalytic behavior. This feature disappears after a few hundred hours of exposure, and a marked decrease of the rate of reaction is then observed. We have shown that no relation exists between these variations of the reaction rate and the variation of UV absorption of films. HCl is formed in the reactions of photooxidation and photoelimination. The autocatalysis and the autoinhibition are favored when the accumulation of HCl is itself favored.

INTRODUCTION

As soon as the first articles on PVC photooxidation were published, some difficulties of analysis were apparent, due to the probable catalytic effect of HCl formed in the reaction [1] and the

competition between the oxidation reaction responsible for the chain scission which leads to the lowering of mechanical properties, and the "zip" dehydrochlorination responsible for the formation of polyconjugated sequences which leads to discoloration and crosslinking. This competition has been particularly studied by sol-gel analysis [2, 3] supplemented by microanalysis of the different fractions [4, 5]. It has been shown that if the HCl evolution is accelerated in the presence of oxygen, in contrast, the average length of the conjugated species, and the extent of crosslinking are limited. The literature dealing with analysis of the degradation products is relatively abundant [4-6]; in contrast, the kinetic data are rare and frequently unreliable, essentially for two reasons. (1) Many studies are based on the measurement of HCl evolution, whereas it has been shown that the polymer partially retains HCl [7] and that HCl can react with polyenes via photochemical readdition [8]. (2) The photochemical behavior of the PVC is strongly perturbed by traces of residual solvent, which has been shown by Kamal [9] to have a sensitizer effect.

We have studied the PVC photooxidation by means of IR and UV spectrophotometry. Some results obtained with films prepared by casting of solutions and carefully purified are reported in this paper. By UV spectrophotometry, we can detect the conjugated polyenes. In our case, the methods of interpretation of spectra which have been used in the case of thermal degradation [10] become inapplicable due to overlapping of "pure" polyene bands -(CH=CH)_n with the oxidized polyene bands [for instance O=C-(CH=CH)_{n-1}] and particular effects in the solid state, i.e., chain folding which leads to a hypsochromic shift due to the rupture of coplanarity, overlapping of the pi electron clouds in aggregate of polyenes which leads to a bathochromic shift [11], and polyene-HCl charge-transfer complexes with strong displacement of the absorption band from UV to visible range.

The problem of quantitative analysis of polyenes is therefore very complex, but we shall suppose that the modification of the absorption spectrum between 250 and 500 nm reflects the evolution of the polyene length distribution during the exposure to UV radiation.

IR spectrophotometry can be used to follow the formation of oxygenated groups, especially C=O and -O-C=O groups. All authors have observed the predominance of a peak located at $1715\text{-}1720\text{ cm}^{-1}$ attributed to α -methylene ketone [5] or to carboxylic acid [12] and which, more probably, results from band overlapping of the two species, the acid resulting from the ketone photooxidation [13].

The molar absorbances of the analyzed groups are particularly high, (ϵ_{max}) $\geq 30,000$ liter/mole-cm for the polyenes in the UV range, and $\epsilon_{\text{max}} = 200\text{-}600$ liter/mole-cm for the CO groups in the

IR range), so that we have a very sensitive method for the study of chemical evolution. Thus, in films analyzed by IR transmission, we can detect less than one CO group per 10 macromolecules and less than one triene group per 100 macromolecules.

It is easy to demonstrate that the contribution of the $-\text{CH}_2-\overset{\text{O}}{\underset{|}{\text{C}}}$ groups to the UV absorption is negligible, their molar absorbance being smaller than 50 liter/mole-cm in the 250-500 nm range. The very short time needed for the measurement and the nondestructive nature of the measurements permit the accumulation of experimental data and, therefore, a realistic appreciation of their dispersion. We studied successively the influence of film thickness and temperature on the photooxidation kinetics.

EXPERIMENTAL

Polymer

The polymer was an industrial "suspension" sample, used without any chemical or thermal treatment, $\overline{M}_w = 71,000$; $\overline{M}_w/\overline{M}_n = 1.90$.

The powder was purified by double reprecipitation: tetrahydrofuran (THF)-water and THF-methanol.

The initial concentration of CO groups (esters absorbing close to $1740-1750\text{ cm}^{-1}$) is $[\text{CO}] = 0.12$ group per macromolecule, taking $\epsilon_{\text{CO}} = 570$ liter/mole-cm. The initial concentration of conjugated trienes (absorbing at 275 nm in UV) is $[\text{T}] \leq 1$ group per 100 macromolecules, taking $\epsilon_{\text{T}} = 35,000$ liter/mole-cm.

Films

The films were prepared by casting solutions of 5 g PVC into 100 cm^3 of THF. It was necessary to control the hygrometry and the rate of evaporation of solvent during casting for the sake of good optical quality and very limited turbidity. The film transmission should be greater than 80% in the near-UV range.

THF was stabilized by a chemical phenolic antioxidant (2, 6-tert-butyl-4-methylphenol) which prevents peroxidation, especially the attack of unsaturated groups initially present in the polymer. The residual THF could be detected in the IR at 1060 cm^{-1} (Fig. 1). The antioxidant accumulating in the film during evaporation of solvent could be detected in the UV at 280 nm (Fig. 2). The films were purified by ether extraction in a Soxhlet apparatus. The residual diethyl ether was eliminated by heating at $40-60^\circ\text{C}$ under vacuum.

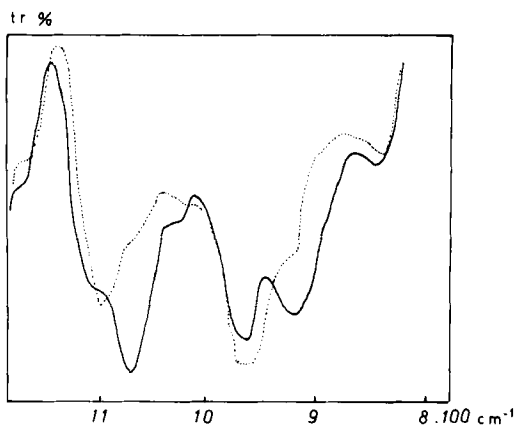


FIG. 1. IR spectra of film: (—) before extraction (THF band at 1060 cm^{-1}); (···) after extraction.

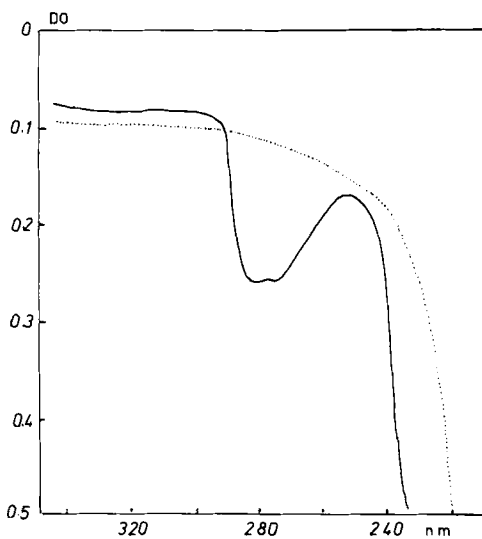


FIG. 2. UV spectra of film: (—) before extraction (phenol band at 280 nm); (···) after extraction.

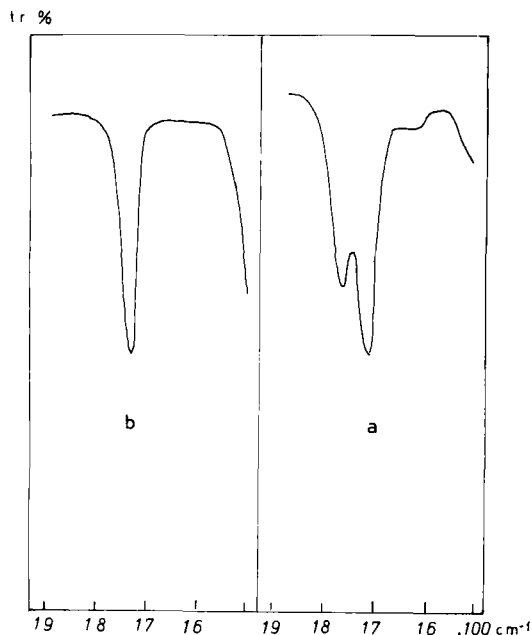


FIG. 3. CO band at $1700\text{--}1800\text{ cm}^{-1}$ in photooxidized films: (a) purified film; (b) nonpurified film.

The efficiency of the purification was verified by the following criteria. For THF, disappearance of the 1060 cm^{-1} band (Fig. 1). No peak at 1770 cm^{-1} appears in photooxidation (Fig. 3) (CO groups of γ -butyrolactone resulting from the THF photooxidation [14]). For antioxidant, disappearance of the 200 nm band (Fig. 2). The optical density (OD) at 280 nm obeys the Beer-Lambert Law, $\Delta OD/\Delta e = cte$ where e is film thickness). In the case of incomplete purification, the absorption of residual antioxidant should lead to a deviation from linearity. The absorbance of the studied bands is high [ϵ_{CO} (butyrolactone) = 600 liter/mole-cm , ϵ_{max} (phenol) = $1500\text{ liter/mole-cm}$], so that this method of control has a great sensitivity.

The film thickness is measured with a micrometer (precision $\approx 1\ \mu\text{m}$); for thicknesses smaller than $50\ \mu\text{m}$, we can utilize the optical density of the IR peak ν_{CH_2} at 2920 cm^{-1} :

$$e_{\text{cm}} = OD_{2920\text{ cm}^{-1}}/172$$

with a routine spectrophotometer, $\Delta e/e = 6\%$.

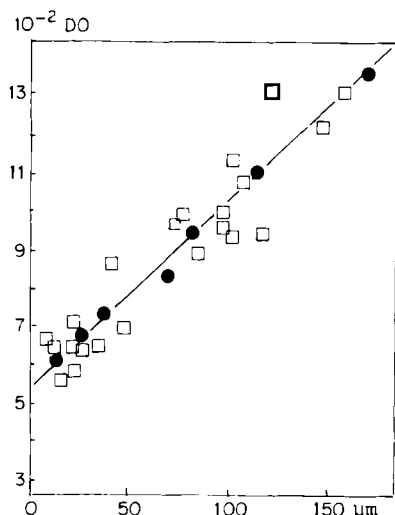


FIG. 4. Initial optical density at 300 nm vs. film thickness.

A set of films is retained for the UV exposure only if all the samples have the same absorption in the UV range. We can see, for instance in Fig. 4, how seven samples were selected from about 30 for the study of the influence of thickness. Their absorption was measured at 300 nm.

Reactors

The photochemical reactors were equipped with an Osram L40W70 or L20W70 fluorescent lamp emitting in the range 300-450 nm with a maximum at about 365 nm.

The intensity was measured by potassium ferrioxalate actinometry and adjusted by action on the supply voltage of the light source. The exposure was made in air; the temperature was constant to $\pm 1^\circ\text{C}$.

EFFECT OF FILM THICKNESS

Seven films of thicknesses between 16 and 175 μm were reacted under the following conditions: temperature, 20°C ; light intensity, 25×10^{18} photons/cm²-hr; total duration of exposure, 800 hr. We followed the change in OD_{CO} at 1720 cm^{-1} and OD_{UV} at 275, 300, 320, and 350 nm (polyenes from $n = 3$ to $n = 6$).

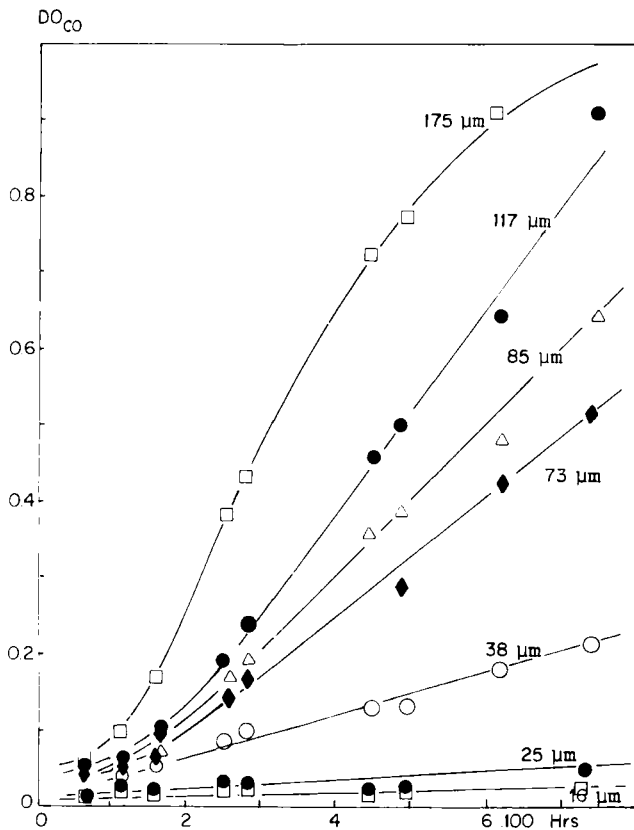


FIG. 5. Optical density of CO peak vs. exposure time for films of 16, 25, 38, 73, 85, 117, and 175 μm thickness.

From the curves of OD_{CO} versus time (Fig. 5), we determined the initial rate:

$$V_{i\text{CO}} = (I/e)[d(\text{OD}_{\text{CO}}/dt)]_{\text{th}}$$

and the maximal rate V_{MCO} . The curves of OD_{CO} versus time show an inflection point which becomes more pronounced as the film thickness increases. We can see on the plots of $V_{i\text{CO}}$ and V_{MCO} versus thickness (Fig. 6) that the initial rate is independent of the thickness while the maximum rate increases strongly between 30 and 50 μm .

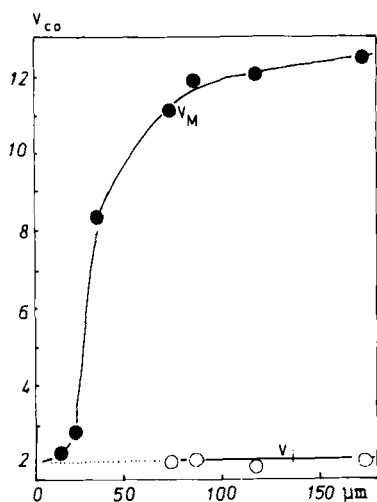


FIG. 6. Maximal rate and initial rate of CO formation vs. thickness.

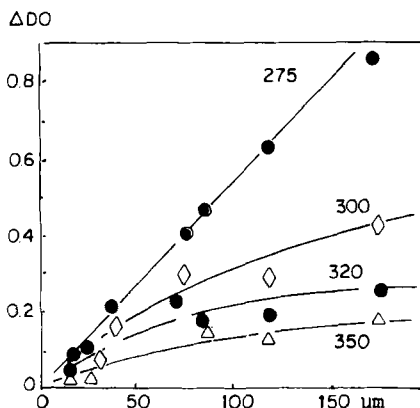


FIG. 7. Overall increase of optical density at 275, 300, 320, and 350 nm after 765 hr of exposure vs. thickness.

In Fig. 7, we have plotted the total increase of optical densities in UV after 765 hr of exposure versus thickness. The relative variation of OD is much smaller as the film thickness increases and the wavelength increases. This can be interpreted as it follows: the

concentration of conjugated trienes is approximately the same in all samples, but the concentration of larger polyenes is much lower in the thicker films.

The smaller variations in UV absorption correspond to the higher rates of formation of CO groups. It is therefore impossible to attribute the variations of photooxidation rates to the variations of UV absorption. Moreover, we have measured the quantum yield in CO groups Φ_{CO} , taking into account the absorption variations in the spectral range of photosensitivity of polymer (300-350 nm). Plots of Φ_{CO} versus time of exposure (Fig. 8) show a sharp maximum which denotes a very particular photochemical behavior. The initial autoacceleration and the "final" autoinhibition are both favored when the thickness is high. We have found only one explanation: their kinetic behavior is controlled by the diffusion of a reactant from the sample to the atmosphere. In a thin film, the formation of this reactant is too low to compensate this loss by diffusion and this particular behavior is not observed. When the thickness of film becomes larger than a critical value (in our case, about 30 μm), accumulation of the reactant becomes possible, and we observe the inflection point on the curves of OD_{CO} versus time.

For the initial autoacceleration, the catalytic effect of HCl on the oxidation, studied in the early 1950's, comes to mind. We have confirmed that gaseous HCl in atmosphere gives an initial acceleration,

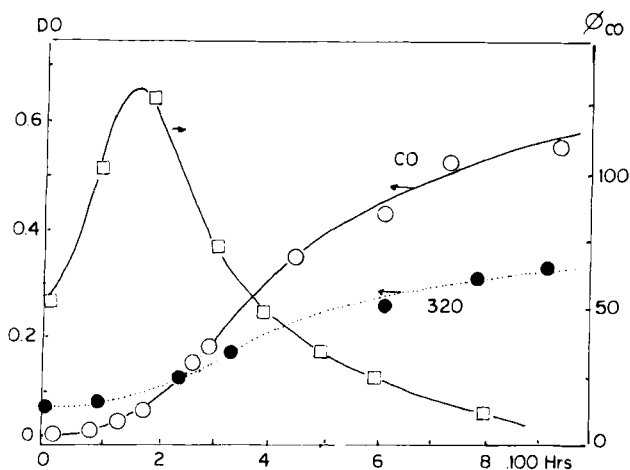


FIG. 8. Plots of (○) OD_{CO} , (●) OD_{uv} at 320 nm, and (□) Φ_{CO} (quantum yield in CO) vs. time for 73 μm film.

whereas an acid acceptor like lead stearate suppresses the autocatalysis. Simultaneous study of the change in carbonyl concentration and the UV spectrum show that HCl acts selectively on the oxidation reaction.

Two interpretations have been proposed. In the first, HCl acts as a chain transfer agent, reacting with a radical such as $\text{ROO}\cdot$ to give a very reactive chlorine radical [1]. In the second, HCl solubilizes metallic impurities, giving metallic salts whose catalytic effect on oxidation reactions is well known [15]. The actual data on bond dissociation energies permit us to invalidate the first hypothesis: $D_{\text{HCl}} = 102$ kcal/mole, whereas D_{RH} in a saturated polymer is smaller than 95 kcal/mole. Thus, we cannot consider HCl as a good hydrogen donor. Our experimental data on different resins at different degrees of purification allow us to invalidate the second hypothesis, also. The autocatalytic behavior seems independent of the metallic trace impurities in the industrial samples. It is noteworthy that the autoinhibition effect also exists in the HCl photoelimination in vacuo and is even more marked than in an oxygen atmosphere [16]. Many authors have interpreted this phenomenon as follows. The irradiation creates conjugated polyenes which are concentrated in a thin layer at the incident surface. As the polyenes are strongly absorbant this layer acts as a protective skin which prevents subsequent photodegradation of the internal zones. Our results show that this hypothesis can be rejected, at least in the present case, for two reasons. The initial transmission of the samples is very high ($> 80\%$ in the near-UV); therefore, the repartition of the degradation products in the thickness of the film must be quasi homogeneous. This invalidates the hypothesis of a high concentration of polyenes close to the exposed surface. Also, the UV absorption variations are too weak to give the observed autoinhibition effect. For the example given in Fig. 8, we can see that from 250 to 850 hr of exposure, the CO formation rate is divided by 3, whereas the UV absorption varies approximately from 13% to 32%, i.e., the light intensities which is transmitted by the film varies from 75% to 56%. This variation of light transmission should lead in the worse case to a reduction of the rate by a factor of 1.3. On the other hand, we can observe in Fig. 5 that the autoinhibition effect is more pronounced in the 175 μm film than in thinner films, whereas the relative increase in UV absorption is proportionately stronger. The effect of film thickness suggests that the autoinhibition effect is also controlled by diffusion of HCl out of the sample and therefore that HCl plays a role in the autoinhibition.

EFFECT OF TEMPERATURE

We exposed 60 and 80 μm films in seven reactors differing only in temperature, the other conditions being light intensity, 17×10^{18}

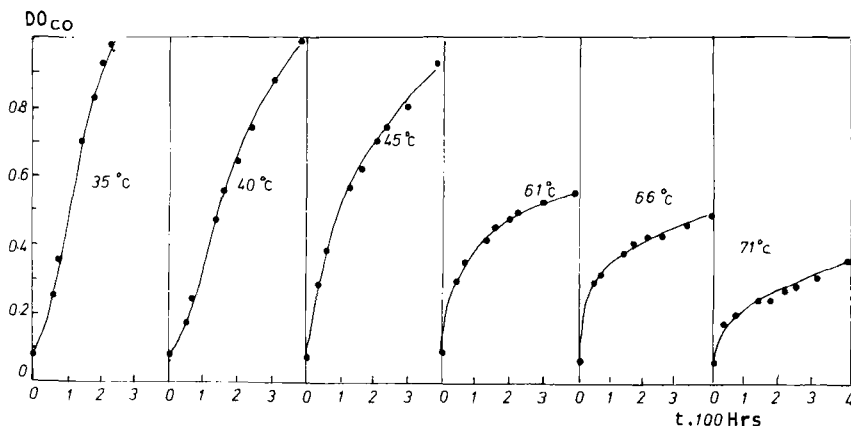


FIG. 9. Optical density of CO peak vs. time for 80 μm film at different temperatures: 35, 40, 45, 61, and 71°C.

photons/cm²-hr; maximum and minimum temperature, 71 and 35°C, respectively; total duration of exposure, 500 hr.

We have followed the change in OD_{CO} (Fig. 9) and observed a disappearance of the initial autocatalytic effect at a temperature higher than 45°C and a marked decrease in overall yield in CO when temperature increases. For instance, the number of CO groups formed after 500 hr exposure at 71°C is five times lower than at 35°C. We have characterized the kinetics of CO group formation by the initial rate: V_{iCO} , the maximal rate V_{MCO} , and a "final" rate V_{FCO} measured between 400 and 500 hr exposure.

In Fig. 10 we have plotted $\ln V_{MCO}$ and $\ln V_{FCO}$ versus the reciprocal absolute temperature for the 80 μm film and the ratio V_{MCO}/V_{FCO} versus $1/T$ which characterizes the autoinhibition effect for the 60 and 80 μm films.

The apparent activation energies are approximately $E_{M80} = 4\text{kcal/mole}$ (maximal rate), $E_{F80} = -9.5\text{kcal/mole}$ and $E_{F60} = -7.5\text{kcal/mole}$ (final rates). These results and Fig. 10 confirm that the autoinhibition effect is markedly stronger for the thicker films.

The disappearance of the autocatalytic effect can be explained as follows. The activation energy of the HCl migration process is greater than the activation energy of this formation process; thus, a temperature increase favors the HCl diffusion. Above a critical temperature, which in this case is near 45°C, accumulation of HCl

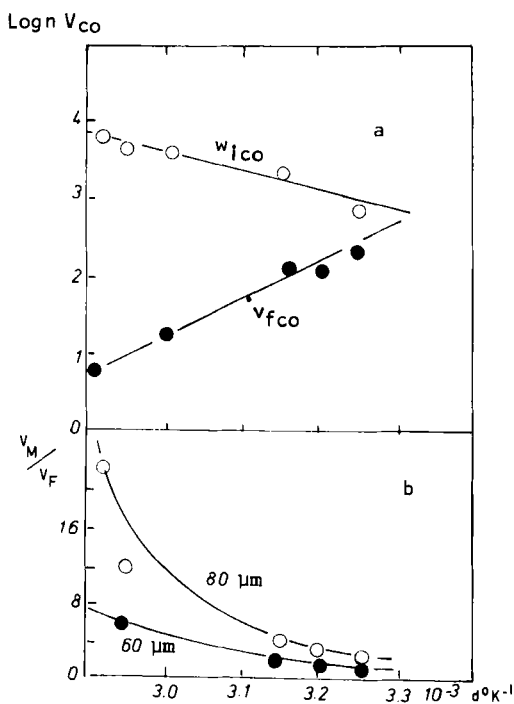


FIG. 10. (a) Arrhenius plots for maximal and "final" rate of CO formation for 80 μm film; (b) $V_{\text{MCO}}/V_{\text{FCO}}$ vs. reciprocal absolute temperature for 60 and 80 μm films.

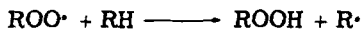
in the film becomes impossible and we do not observe the autocatalysis. The autoinhibition effect is favored by an increase in film thickness, but in contrast with the autocatalytic effect it is strongly activated by a temperature increase. It is actually difficult to interpret this behavior. An analysis of post-irradiation effects [13] showed that the photooxidation process is complicated by a "zip" HCl thermoelimination. This last reaction can play a significant role in the production of autostabilizing structures.

PROPOSED MECHANISMS

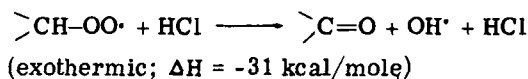
We shall propose an interpretation of autocatalysis and autoinhibition phenomena based on observed behavior and literature data. A detailed analysis of mechanism will be presented in a forthcoming paper.

Autocatalysis

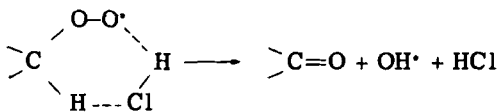
We have shown that HCl acts in the proper oxidation reaction. On the other hand, analytical and kinetic data are unfavorable for the hydroperoxide formation step:



We suggest that HCl catalyzes the unimolecular decomposition of peroxy radical in ketone and hydroxy radical:



We can suppose the existence of a six-membered transitional complex:



It is important to note that this process does not involve a chain scission. The observed decrease of molecular weight is attributed to secondary reactions, essentially photolysis and photooxidation of ketones.

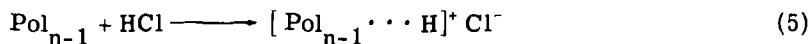
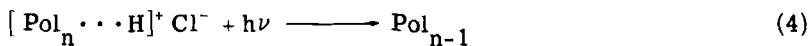
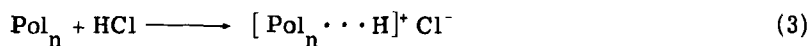
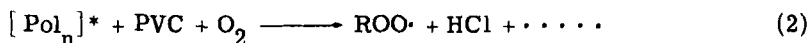
Autoinhibition

We have shown that HCl plays also a role in the autoinhibition effect. We propose a mechanism of inhibition of the polyenes photo-reactivity by formation of a charge-transfer complex (CTC) with HCl.

As polyenes are the principal photochemical initiators for PVC, we shall observe an inhibition if: HCl is in excess, i.e., if the conditions previously described favor the HCl accumulation and if the time of irradiation is sufficient to attain the high concentration needed for the process or if the CTC is effectively inert to photooxidative attack. We have found that (1) the absorption band of CTC lies in the visible range, near 500 nm, and the corresponding energy of the excited state is about 57 kcal/mole, too low for a sensitization of polymer by a

transfer process. (2) The excited state structure is not biradicaloid and, therefore, can be less favorable than the classical triplet structure to an oxygen attack. (3) The ground state structure of CTC is also probably unfavorable for an attack by photoexcited species of oxygen. We cannot say that the CTC is totally photostable, but its only mode of photoreaction is probably the readdition of HCl, lead to a polyene shortening.

The scheme summarized in Eqs. (1)-(5) is proposed where Pol_n denotes $(-\text{CH}=\text{CH}-)_n$. The sequence (1)-(2) is favored at the beginning of exposure or when the conditions for HCl accumulation are unfavorable. The sequence (3)-(5) will be favored when the HCl accumulation is itself favored



CONCLUSION

The peculiarity of the photochemical behavior of PVC can be explained by the double role of HCl formed in the reactions. As an inhibitor for the initiation step, forming a CTC, HCl prevents the polyenes from reaching the photoexcited state responsible for the initiation. Concurrently, HCl acts as a catalyst for the propagation of the oxidation chain.

The interpretation of kinetic data is complicated by diffusion of HCl out of the sample. The peculiarities of PVC behavior are evident when conditions are favorable for HCl accumulation in the films (thick films and low temperatures).

ACKNOWLEDGMENT

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REFERENCES

- [1] D. Druessedow and C. F. Gibb, Polymer Degradation Mechanisms, (Nat. Bur. Std. Circ. 525), Washington, D. C., 1953, p. 69.
- [2] A. S. Kenyon, in Polymer Degradation Mechanisms, (Nat. Bur. Std. Circ. 525), Washington, D. C., 1953, p. 81.
- [3] H. H. Jellinek, Pure Appl. Chem., **4**, 419 (1962).
- [4] J. Petit and Zaitoun, C. R. Acad. Sci. (Paris), **C256**, 2610 (1963).
- [5] K. P. S. Kwei, J. Appl. Polym. Sci., **7**, 1075 (1969).
- [6] A. V. Karyakin, G. V. Grishin, and B. D. Kurkin, Polym. Sci. USSR, **7**, 429 (1965).
- [7] A. Guyot and M. Bert, J. Appl. Polym. Sci., **17**, 753 (1973).
- [8] E. D. Owens and J. L. Williams, J. Polym. Sci. Polym. Chem. Ed., **12**, 1933 (1974).
- [9] M. R. Kamal, M. M. El Kaissy, and M. M. Avedesian, J. Appl. Polym. Sci., **16**, 83 (1972).
- [10] G. Palma and M. Carezza, J. Appl. Polym. Sci., **16**, 2485 (1972).
- [11] A. A. Berlin, Vysokomol. Soedin., **A13**, 276 (1971).
- [12] G. Scott and M. Tahan, Eur. Polym. J., **11**, 535 (1975).
- [13] J. Verdu, Thesis, Paris, 1976.
- [14] J. Malac, Z. Zellinger, and E. Simunkova, J. Polym. Sci. A-1, **7**, 1893 (1969).
- [15] G. Scott, Atmospheric Oxidation and Antioxidants, Elsevier, New York-Amsterdam, 1965, p. 307.
- [16] W. H. Gibb and J. R. McCallum, Eur. Polym. J., **8**, 1223 (1972).

DISCUSSION

Dr. Tran (Centre National de la Recherche Scientifique, Villeurbanne): You have shown a complex between hydrochloric acid and a peroxy radical. Can you explain how you observed this complex?

Dr. Verdu: I have said that it was only an hypothesis. We have not proved the actual occurrence of such a complex. We have only a set of analytical and kinetical data which suggest a mechanism of this kind. The catalytic effect of HCl would operate on the decomposition of peroxy radicals. At first, in the classical oxidation process, the rate-controlling step is hydrogen abstraction from the polymer. But the activation energies generally observed for such a step are definitely higher than the one we have observed, which is almost zero. For instance, in the photooxidation of polyethylene or polypropylene, the activation energies are between 8 and 13 kcal/mole. On the other hand, the analytical study shows that we get mostly ketone groups in

the photooxidation products, and then all the groups produced by photooxidation of these ketones, i.e., chiefly acid, peracids, or peresters. In the usual case, after the hydrogen abstraction one gets a hydroperoxide, and the most probable reaction is the scission of the O-O bond which produces an alkoxy radical; the most probable reaction here is the formation of an aldehyde. There is also the possibility of alcohol formation after a hydrogen abstraction step. We have, however, not observed a large amount of aldehyde and alcohol in the products under the conditions we have studied. We get mostly ketones, and it is rather difficult to explain the formation of ketones with the conventional oxidation mechanism. We have shown that the mechanisms already proposed to explain the catalytic effect of HCl are not convincing, and we suggest our mechanism, but at the present time, it remains essentially speculative.

Mr. Stapfer (Sté Metrastat, Paris): In view of these reaction mechanisms which have repeatedly been proposed in the literature, would it not be possible during the kinetic study of the phenomenon to look at the effect of hydroperoxide decomposers? You said that you have already used phenolic antioxidants. I do not know to what extent and how long these phenols remain in the film, but in the practice of the stabilization of PVC to light, for example, the best results are obtained by precisely using phenolic antioxidants in addition to organotin carboxylates as heat stabilizers. What then is the precise role played by the antioxidant or a hydroperoxide decomposer in PVC?

Dr. Verdu: At first, I think that we have good analytical evidence for the almost complete consumption of the phenolic antioxidant in our films, because the UV peak at 280 nm for phenolic compounds is rather intense; it corresponds to the aromatic ring of the phenol; its extinction coefficient is about 1500 liter/mole-cm, so it is a sensitive test. I think the problem of the activity of phenolic antioxidants is very complex. The phenolic antioxidants are active on the oxidation chain reactions, but they are also photoinitiators. In the case of PVC they will act selectively on the oxidation chain reaction. But the oxidation limits the length of the polyene sequences, so that by acting on the oxidation, you have a change to favor the formation of long polyene sequences. Concerning the peroxide decomposers, it is difficult to give an answer now. I have no data for predicting their behavior (for instance of thiols) on the course of PVC photooxidation.

Dr. Wirth (Ciba-Geigy, Marienberg, West Germany): An additional comment to Dr. Stapfer's question is that the kinetic chain lengths in the photooxidation or autooxidation of PVC are rather short. Therefore, phenolic antioxidants do not have such a tremendous activity as they have in polyolefins, for instance. Would this fit in with that question?

Mr. Stapfer: I will not repeat the whole of my previous question, but the problem in polyolefins is quite different. If we want to protect polyolefins against photodegradation, two kinds of antioxidants are needed: first, a phenolic antioxidant which will trap these alkoxy and RO radicals and also a sulfur-containing compound to act as a hydroperoxide trap or decomposer. In PVC this synergism between thio compounds and phenols does not appear to exist. However, the phenolic antioxidant alone with some organotin carboxylates improves the stability considerably.

Dr. Wirth: The thermal stability?

Mr. Stapfer: No, the photostability. My question was, what is the effect of these various components, the phenolic antioxidants or possibly some selected sulfur compounds, taken alone? That question seems to remain unanswered.

Dr. Wirth: I should like to refer to a paper published by Svoboda, who carried out systematic investigations with the various antioxidants, type I and type II, (i.e., hydroperoxide decomposer and kinetic antioxidant) in the light stabilization of PVC. He found that both of them are active, but that the tremendous effect of phenolic antioxidants known for polyolefins cannot be obtained.

Mr. Stapfer: Dr. Verdu is, of course, in an ideal position to measure these effects kinetically. He has an experimental device which allows him to look at the finer points, which is what makes this procedure particularly interesting.