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MECHANISM OF PHOTOCHEMICAL DEHYDROCHLORINATION OF POLY(VINYL CHLORIDE)

M. A. ZHURAVLEV and V. B. IVANOV*
Institute of Chemical Physics, U.S.S.R. Academy of Sciences, 4 Kosygin Street, Moscow, U.S.S.R.

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Abstract—The paper deals with the effect of the light wavelength and plasticizers on the formation of polyenes and evolution of HCl, as well as on accumulation of alkyl and polyenyl radicals, during photolysis of poly(vinyl chloride) (PVC). The total number of polyenes and the distribution of their lengths are quantitatively analyzed by numerical modelling of the recorded spectra with the aid of the absorption spectra of model compounds. The dependences of the quantum yield of dehydrochlorination on the wavelength are determined. The correlation between the dehydrochlorination rate and steady-state concentration of radicals, as well as the agreement between the photochemical sensitivity spectra of an intermediate and the absorption spectra of radicals, suggest that radicals are photochemically active intermediate products of the dehydrochlorination. The constants of the individual stages are evaluated on the basis of ideas about the photochain character of the process in rigid PVC.

INTRODUCTION

Dehydrochlorination accompanied with the formation of conjugated double bonds in macromolecules is one of the main processes in photoageing of poly(vinyl chloride) (PVC) [1]. We have shown that alkyl and polyenyl radicals accumulating during the induction period of dehydrochlorination may be the intermediate products of the reaction [2]. The aim of this work is to establish the mechanism of photochemical dehydrochlorination of PVC. Attention is paid mainly to the quantitative dependences of the process rate on the intensity and spectral distribution of light and on physical properties of polymers.

EXPERIMENTAL PROCEDURES

Samples of bulk, suspension and emulsion commercial PVC of grades M-64 (U.S.S.R.), Scovinyl S (G.D.R.), and Scovinyl E (G.D.R.), respectively, were used. Films 8 or 40 μm thick were prepared by slow evaporation of solvent from a polymer solution in dichlorethane cast on glass. Dibutyl sebacinate used in some cases as a plasticizer was purified by distillation under reduced pressure and introduced into the polymer solution.

The samples were irradiated in vacuum (residual pressure $\simeq 0{,}1$ Pa) at room temperature ($20 \pm 2°$) with low-pressure (DB-60) and high-pressure (DRSh-1000 or SVD-120) Hg lamps. Light with the required wavelength was isolated by glass filters alone or combined with liquid and gas filters: $\lambda = 265$ nm, $I = 9.04 \times 10^{-4}$ J/cm^2·sec, UFS-2, quartz "KI" with a thickness of $1 = 2$ cm, Cl$_2$ under pressure 0.1 MPa and $1 = 5$ cm; $\lambda = 280$ nm, $I = 6.52 \times 10^{-4}$ J/cm^2·sec, UFS-1, Cl$_2$ with $1 = 1.5$ cm and PS film with $1 = 10\,\mu$m; $\lambda = 313$ nm, $I = 1.7 \times 10^{-3}$ J/cm^2·sec, ZhS-3 and UFS-2; $\lambda = 334$ nm, $I = 1.33 \times 10^{-3}$ J/cm^2·sec, standard combined liquid light filter [3]; $\lambda = 365$ nm, $I = 3.91 \times 10^{-3}$ J/cm^2·sec, BS-7 and UFS-6; $290 < \lambda < 460$ nm, $I = 2.6 \times 10^{-2}$ J/cm^2·sec, FS-6. As a radiation source ($\lambda = 254$ nm, $I = 3.1 \times 10^{-4}$ J/cm^2·sec) use was made of a DB-60 lamp without additional filters. The light intensity was changed by placing metal meshes between lamp and sample. For light with $\lambda = 254$ nm, thick quartz plates were also used. The intensity was determined using a ferrioxalate actinometer and a thermocouple [3].

The rate of HCl evolution was determined potentiometrically on a pH-121 device. The absorption spectra in u.v. and visible regions were recorded on Specord UV-Vis and Specord M-40; the ESR spectra were recorded on ESR-V instrument.

The distribution of lengths of polyenes was analyzed by numerical modelling of the absorption spectra. An individual spectrum of the jth polyene was represented as a superposition of 4 or 5 G curves:

$$\epsilon_j(\lambda) = \sum_{k=1}^{4\text{ or }5} \epsilon^{\max}_{k=1} \frac{(\Delta\lambda^{\exp}_{1/2})_{kj}}{(\Delta\lambda_{1/2})_{kj}} \exp\left(- \frac{\ln 2(\lambda - \lambda^{\max}_{kj})^2}{(\Delta\lambda_{1/2})^2_{kj}} \right),$$

where: $\epsilon_j(\lambda)$ is the analytical function characterizing the absorption band contour of polyene with a chain length of j; $\epsilon^{\max}_{kj}$ is the value of the jth G curve maximum; $(\Delta\lambda_{1/2})_{kj}$ is the half-width of this curve; and $(\Delta\lambda^{\exp}_{1/2})_{kj}$ is the half-width of the corresponding band in the experimental absorption spectrum. The surface area under the theoretical absorption band $\epsilon_j(\lambda)$ was normalized on the surface area under the experimental spectrum of the corresponding polyene [4] for H—(CH=CH)$_n$—H molecules in isooctane,

$$\int_0^\infty \epsilon_j(\lambda)\,\mathrm{d}\lambda = \sum_{k=1}^{4\text{ or }5} \epsilon^{\max}_{kj} (\Delta\lambda^{\exp}_{1/2})_{kj} \sqrt{\pi/\ln 2}.$$

The spectra not already published [4] were plotted by following a published procedure [5]. The concentration of polyenes of different lengths n was found with the aid of an iteration approximation based on the least squares method [6]. The most probable distribution of concentrations was found by minimizing the function

$$U = \left[\sum_{i=1}^{m} \omega_i \left\{ D(\lambda_i) - l \sum_{j=1}^{n} \epsilon_j(\lambda_i) c_j \right\}^2 \right] = \min,$$

where $D(\lambda_i)$ is the optical density in the PVC spectrum at wavelength λ_i, l is the thickness, c_j is the concentration of polyene with chain length j, ω_i is the statistical weight of the ith measurement. For ω_i, use was made of the reciprocal values of optical density dispersions. During calculation, not only concentrations of polyenes were varied but also the positions and widths of their spectra in order to attain the best coincidence of theoretical and experimental spectra.

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*To whom all correspondence should be addressed.

The agreement between the calculated value of the total concentration of double bonds and the experimental concentration of liberated HCl, as well as a uniform decrease of c_j with increasing j (the closeness of c_{j-1}/c_j and c_j/c_{j+1}) were the additional criteria of the correctness of the estimations. The spectra were modelled on SM-4 and Electronica DVK-2 computers using a working program based on Fortran-IV language.

RESULTS

Composition of polyenes and kinetics of their formation

Figure 1 illustrates the experimental and calculated spectra of polyenes formed during photochemical dehydrochlorination of PVC under steady-state conditions and Table 1 shows the calculated concentrations of polyenes. Noting the good agreement between the calculated and experimental spectra as well as the fact that polyene concentration (4.8×10^{-2} mol/l with $n = 2 - 12$) is very close to the concentration of liberated HCl (5.3×10^{-2} mol/l), one may conclude that the calculation characterizes rather well the distribution of polyenes formed during photochemical dehydrochlorination of PVC making it possible to determine the absolute rates of their accumulation.

The kinetics of polyene accumulation have some specific features.

(1) When light intensities are not too great ($i < 10^{-2}$ J/cm^2·sec), a clearly pronounced induction period is observed after which dehydrochlorination proceeds at an almost constant rate (Fig. 2). The length of the induction period depends on the polymer type and spectral distribution of light whereas dehydrochlorination rates virtually coincide for polymers of different types.

(2) Length distribution of polyenes is constant up to high conversion during the steady-state stage of the process both for rigid and plasticized PVC. At the same time, length distribution of polyenes depends on the spectral distribution of light and on the presence of oxygen.

(3) On irradiation of the sample with polychromatic light, the rate is proportional to the radiation intensity in the short-wavelength region ($\lambda \simeq 250$ nm) whereas, with increasing intensity of the long-wavelength component ($\lambda > 300$ nm), the rate reaches a constant limit more than twice the rate attained upon irradiation with monochromatic light ($\lambda \simeq 250$ nm).

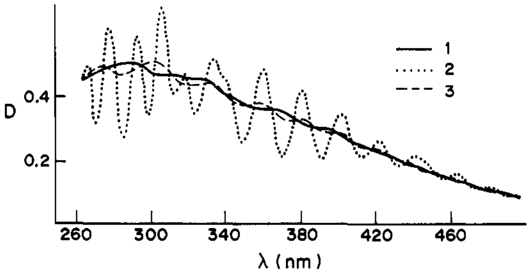

Fig. 1. Absorption spectra of polyene sequences in PVC: 1—experimental, irradiation with light of $\lambda = 254$ nm; 2—calculation with the use of model spectra of $H-(CH=CH)_n-H$ molecules and 3—the same with additional shift and spectral broadening.

Table 1. Length distribution of polyene sequences on irradiation of PVC with light ($\lambda = 254$ nm)

n	$c_n \times 10^3$ (mol/l)	c_n/c_{n+1}	α_n	$w_n \times 10^3$ (mol/l·hr)
2	7.38*	2.13	0.49	2.46
3	3.46	1.83	0.23	1.15
4	1.89	1.93	0.13	0.63
5	0.98	1.77	0.065	0.32
6	0.55	1.72	0.036	0.18
7	0.32	1.46	0.021	0.11
8	0.22	1.47	0.014	0.073
9	0.15	1.49	0.0098	0.049
10	0.10	1.50	0.0066	0.033
11	0.066	1.57	0.0044	0.022
12	0.042	—	0.0028	0.014

*Calculated by the absorption spectra since the bands of dienes and other polyenes are almost not overlapped.

(4) The quantum yields of dehydrochlorination drop sharply with increasing wavelength in the region $254 < \lambda < 280$ nm (Fig. 3); therefore, the dehydrochlorination rate upon irradiation with light with $\lambda < 300$ nm is negligibly small, even for preliminary destructed samples, as compared with that under the

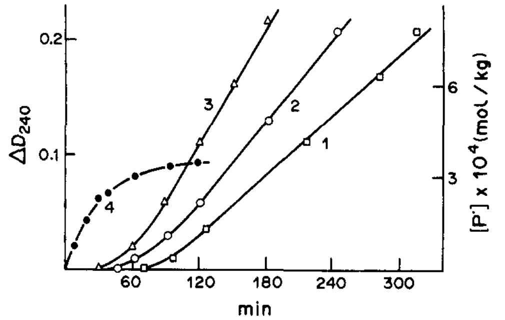

Fig. 2. Accumulation of dienes (1–3) and radicals (4) under the action of light from one lamp ($\lambda = 254$ nm) (1, 4) and simultaneously from two lamps [$\lambda = 254$ and 313 nm (2) or $290 \leqslant \lambda \leqslant 460$ nm (3)] on a PVC film 40 μm thick.

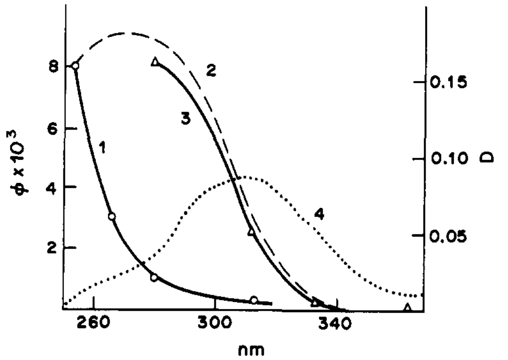

Fig. 3. Quantum yield of PVC dehydrochlorination as a function of wavelength under the action of light from one lamp (1) and from two lamps (2,3) one of which emits light with $\lambda = 254$ nm, and the other with variable wavelength; the contribution of light with longer wavelength is not taken into account (2) and is taken into account (3). 4—The absorption spectrum of the molecular product formed upon irradiation with short-wavelength light.

influence of the complete radiation from a high-pressure Hg lamp.

(5) The rate of dehydrochlorination decreases sharply with introduction of a plasticizer. For instance, the quantum yield of dehydrochlorination of the sample containing 12% of dibutyl sebacinate irradiated with $\lambda = 254$ nm is only 0.0012 whereas for rigid PVC it reaches 0.008.

These specific features of the photochemical dehydrochlorination of PVC indicate that, on irradiation with the polychromatic light of a high-pressure Hg lamp, the line with $\lambda = 254$ nm makes the main contribution. Long-wavelength light with $\lambda > 300$ nm, which by itself does not exert any effect, in combination with short-wavelength light accelerates noticeably the dehydrochlorination (Fig. 2). As the experiment has shown, the effect of long-wavelength light is observed only during simultaneous irradiation but also for alternate irradiation with short- and long-wavelength light. These data and other results discussed above point to the existence of a relatively long-lived intermediate product responsible for photochemical dehydrochlorination of PVC.

Intermediate products of dehydrochlorination

The electron absorption spectra of the samples irradiated with short-wavelength light ($\lambda = 254$ nm) are characterized, in particular, by the presence of a maximum (shoulder) at 310–330 nm. A rise in absorption within the 250–360 nm region during photolysis is accompanied with a weak decrease of absorption in the short-wavelength region (220–250 nm). Absorption in the 250–360 nm region decreases rapidly on irradiation with long-wavelength light (Fig. 4). Other authors [7] attributed this absorption to the formation of dienes and trienes and considered them as intermediate products of photochemical dehydrochlorination of PVC. However, such a mechanism was not confirmed by kinetic data. According to our results, the absorption in the 250–360 nm region can be related to dienes and trienes, since the products being formed are stable in the absence of light in vacuum and in air which suggests their molecular nature but they are readily consumed under the action of ozone reacting at a high rate with conjugated double bonds [8]. These products, however, cannot be considered as intermediates in the photochemical dehydrochlorination of PVC since, after the introduction of a plasticizer, both their steady-state concentration and the formation rate somewhat increase rather than decrease whereas the dehydrochlorination rate drops sharply [9]. The region of spectral sensitivity of the intermediate products obtained in special experiments with two monochromatic light sources (with constant $\lambda = 254$ nm and with variable λ) is additional proof that neither dienes nor trienes are the intermediate products. As follows from Fig. 3, the spectrum is strongly shifted towards short-wavelength as compared with the spectrum of molecular products.

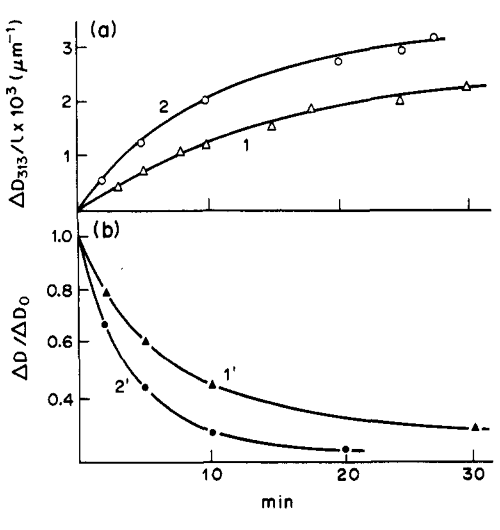

Fig. 4. Kinetics of the formation (a) and consumption of (b) of a molecular product on irradiation of rigid (1,1') and containing 15% plasticizer (2,2') PVC with 254 nm (a) and 313 nm (b) light.

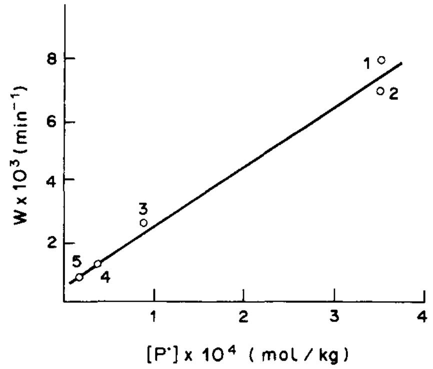

Fig. 5. The ratio between the rate of polyene formation and steady-state concentration of free radicals on irradiation of rigid PVC (points 1,2) and samples containing 2% (point 3), 6% (4) and 10% (5) of dibutyl sebacinate.

The study of the kinetics of accumulation, mutual transformation, and consumption of alkyl and polyenyl radicals shows that these species are intermediate products of the photochemical dehydrochlorination of PVC.

(1) Radicals are formed even in early irradiation stages and their quasi-stationary concentration is attained at a quasi-stationary dehydrochlorination rate (Fig. 2).

(2) The spectrum of light action (Fig. 3) quantitatively corresponds to literature data on the absorption of polyenyl radicals [10].

(3) The introduction of a plasticizer results in a corresponding decrease of steady-state concentration of radicals and the rate of PVC dehydrochlorination (Fig. 5).

(4) On irradiation with long-wavelength light, the ESR spectrum of radicals becomes narrower but it widens when irradiation is performed with short-wavelength light [2] indicating a change of the conjugation chain length in radicals.

(5) The supply of oxygen into a cuvette with a vacuum-irradiated film noticeably decreases the absorption in the long-wavelength region and simultaneously results in rapid decrease of the ESR signal intensity.

The transformation of radicals under the action of light, as follows from the above data, leads to a change of the conjugation chain in radicals but is not accompanied with any noticeable change in the concentration of free valencies. For instance, upon additional irradiation with long-wavelength light, along with short-wavelength light, the initial rate of formation and steady-state concentration of free radicals increase only by approx. 25% whereas the dehydrochlorination rate is doubled. A small rise of the initiation rate upon additional irradiation with long-wavelength light may be related, at least partially, to the initiating action of the molecular product but the contribution of this process is small.

DISCUSSION

Kinetic scheme of dehydrochlorination

The general scheme of photochemical dehydrochlorination of PVC must be based on the above kinetic specific features of the process and also explain the main kinetic trends, including first the proportionality of the steady-state rate to the light intensity and its dependence on the spectral distribution of the light.

Consider one of the simplest schemes which takes into account photochemical propagation of the kinetic chain of PVC dehydrochlorination with the participation of radicals

$$\begin{array}{ll}
\mathrm{X} \to \mathrm{P}^{\bullet} & w_0 \\
\mathrm{P}^{\bullet} \to \mathrm{P}_1^{\bullet} & k_1 \\
\mathrm{P}_1^{\bullet} \to \mathrm{P}_2^{\bullet} & \alpha_2 k_{\mathrm{eff}} \\
 & \\
\mathrm{P}_1^{\bullet} \to \mathrm{P}_{\mathrm{n}}^{\bullet} & \alpha_n k_{\mathrm{eff}} \\
\mathrm{P}_1^{\bullet} \to \mathrm{P}_1 + \mathrm{P}^{\bullet} & k_{\mathrm{p},1} \\
 & \\
\mathrm{P}^{\bullet} \to \mathrm{P}_n + \mathrm{P}^{\bullet} & k_{p,n} \\
\begin{array}{l} \mathrm{P}^{\bullet} \to \\ \mathrm{P}_1^{\bullet} \to \end{array} \left\{ \begin{array}{l} \text{stable} \\ \text{products} \end{array} \right. & \begin{array}{l} k_t \\ k_{t,1} \end{array}
\end{array}$$

where X are the foreign chromophore groups, $P^{\bullet}$ are alkyl radicals, P_n and $P_n^{\bullet}$ are polyenes and polenyl radicals with a chain length of conjugation of *n* units. In the general case, the stages comprised by this scheme are not elementary and include both thermal and photochemical reactions; therefore, the effective constants for all stages must depend on intensity and spectral composition of light and on temperature.

In a quasi-stationary approximation, the rate w_n of polyene formation is determined as:

$$w_n = \alpha_n w_0 \frac{k_1}{k_t + (k_1 + k_t)k_{t,1}/k_{\mathrm{eff}}}. \qquad (1)$$

Since the steady-state concentration (but not the composition) of radicals depends weakly on the intensity of long-wavelength light, one may assume that the effect of this light on dehydrochlorination is caused predominantly by an increase in k_{eff}. If the intensity of the long-wavelength light is very high, the dehydrochlorination rate attains a constant value equal to

$$w_{n,\mathrm{lim}} = \alpha_n w_0 (k_1/k_t). \qquad (2)$$

Since from the experimental data it follows that $w_{n,\mathrm{lim}} \simeq 2w_n$, at *n* equal, for instance, to 7 and using the values of $w_{n=7} = 7.6 \times 10^{-5}$ mol/l·hr, $w_0 = 9.2 \times 10^{-5}$ mol/l·hr, and $\alpha_7 = 0.021$, we obtain from equation (2) $k_1/k_t \simeq 20$. On irradiation with monochromatic light at the same intensity at $\lambda = 254$ nm equal to 3.1×10^{-4} J/cm^2·sec, using the k_1/k_t ratio from equation (1), we have $k_{t,1}/k_{\mathrm{eff}} \simeq 2.5 \times 10^{-2}$. The absolute values of the constants can be found if we assume that $k_{t,1}[P_1^{\bullet}] \gg k_t[P^{\bullet}]$ and that the steady-state concentration of free radicals is $\simeq 10^{-4}$ mol/l. In this case we obtain $k_{t,1} \simeq 1$/hr and, hence, $k_{\mathrm{eff}} \simeq 40$ l/hr.

On irradiation with monochromatic light with $\lambda = 254$ nm, $k_{\mathrm{eff}} = \phi \epsilon_{254} I_{254}$, where ϕ is the quantum yield of $P_1^{\bullet} \to P_j^{\bullet}$ transformation ($2 \leqslant j \leqslant n$), since in rigid PVC all stages are photochemical. At $\epsilon \simeq 10^4$ l/mol·cm and $I = 1.4$ mol/l·hr, we obtain $\phi = 0.7$ in good agreement with literature data on high photochemical activity of polyenyl radicals [11].

Thus, the proposed scheme describes properly the qualitative trends and agrees with the quantitative experimental data available.

CONCLUSION

Photochemical dehydrochlorination of PVC is a photochain process in which the chain propagates as a result of photochemical transformation of alkyl and polyenyl radicals. The photochemical chain length depends on the irradiation conditions and is $v = k_{\mathrm{eff}}/k_t \simeq 40$ units when the wavelength is 254 nm. Therefore, not only plasticizers but other additives influencing the steady-state concentration of free radicals should exert a considerable stabilizing effect. Usual antioxidants, however, cannot be used for rigid PVC because of their low mobility in glass-like polymers and low light resistance.

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