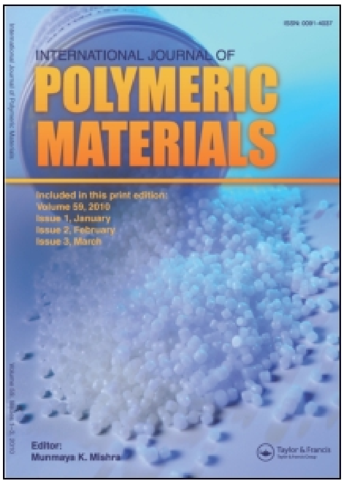

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The General Patterns of Photooxidative Degradation of Aliphatic Polyamides

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A new mechanism for the photooxidation of aliphatic polyamides, which was suggested by one of the authors, is essentially verified by comparing the experimental data described earlier with the exact solution of a corresponding system of differential kinetic equations. For the most interesting particular case of polyamide photooxidation under the action of long wavelength light the solution using a quasi-stationary approximation is justified. In this case the kinetics of changes in the concentrations of the most important intermediate products is represented by a hyperbolic functions.

KEY WORDS Photooxidative degradation, aliphatic polyamides

INTRODUCTION

Some time ago we showed[1] that all known patterns of behavior for the photooxidation of aliphatic polyamides (PA) could best be explained by the generalized kinetic scheme of a fundamentally new mechanism. So far this scheme has no analog among the mechanisms proposed to describe the kinetics of the oxidation of polymers of other classes. The proposed scheme explains 4 arrays of kinetic data and represents the first example of the quantitative treatment of photooxidation within such wide ranges of light wavelength and intensity, and which embraces nearly all conditions of photoaging that are of practical interest.

It is important to note that all kinetic characteristics measured were the same for the two different polyamides (nylon 6 and PA-548). This fact means that some common mechanism exists, and the question concerns only its specific nature.

The suggested generalized scheme is[1]:

Propagation

1. $PO_2^{\cdot} + PA \xrightarrow{+O_2} POOH + PO_2$

2. $PO_2^{\cdot} \rightarrow A + r^{\cdot}$

2′. $PO_2^{\cdot} \rightarrow B + r^{\cdot}$

3. $r^{\cdot} + PA \xrightarrow{+O_2} rH + PO_2^{\cdot}$

4. $A \xrightarrow{+2O_2} K$

4′. $A \xrightarrow{+2O_2} K'$

5. $K + r^{\cdot} \rightarrow PO_2^{\cdot} + S$

5′. $K' + r^{\cdot} \rightarrow PO_2^{\cdot} + S$

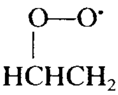
6. $PO_2^{\cdot} + r^{\cdot} \xrightarrow{-O_2}$ termination $+ S$

Initiation

7. $K \xrightarrow{+hh\nu+2O_2} 2PO_2^{\cdot} + S$

7′. $K' \xrightarrow{+h\nu+2O_2} 2PO_2^{\cdot} + S$

8. $PA \xrightarrow{+h\nu+2O_2} 2PO_2^{\cdot} + S$



where $PO_2^{\cdot}$ = peroxide macroradicals $\sim CH_2CONH\overset{O-O^{\cdot}}{\overset{|}{C}}HCH_2\sim$, $r^{\cdot}$ = low molecular radicals (supposedly $HO_2^{\cdot}$ or superoxid anion), A, K, K' = intermediate molecular products, B = the set of final products, S = the scission of the macromolecule. Bear in mind that the relative contribution of the photoinitiation reactions, 7, 7′, 8 depends on the photon energy $h\nu$, and in different modes of photooxidation one of these reactions is prevailing, (for example, long wavelength light is not absorbed by the PA, and under its action reaction 8 does not go). The difference between the modes of photooxidation is determined by the reactions of photoinitiation, while other reactions in this scheme are common for all the modes.

This scheme represents the minimum number of chemical reactions which are necessary to describe the existing experimental data. The preliminary discussion of these reactions is given in References 1–4 together with evaluations of their rate constants. However, the values of these constants vary in their reliability. More reliable are parameters taken from the kinetic data related to the stationary conditions of photooxidation. The missing parameter was evaluated[3] from the kinetics based on a stationary quasi-stationary approximation which supposes that the stationary concentrations of radicals are reached very quickly in comparison to the concentrations of molecular intermediate products. As the correctness of such an approximation is not obvious, calculations of the full system of differential kinetic equations for considering the scheme of chemical mechanism are made. The results of such calculations are given below for the most important case of polyamide photooxidation under the action of long wavelength light (365–440 nm).

CALCULATIONS AND DISCUSSION

In this case[1-3] $k'_7 = k_8 = 0$, and assumes a stationary concentration of the intermediate product A,[3] so that the task is reduced to the solution of this system of differential equations:

$$\frac{d(\mathrm{PO_2})}{dt} = -(k_2 + k'_2)(\mathrm{PO_2}) + k_3(r) + (r)[k_5(K) + k'_5(K')] - k_6(\mathrm{PO_2})(r) + 2k_7I_0(K)$$

$$\frac{d(r)}{dt} = (k_2 + k'_2)(\mathrm{PO_2}) - k_3(r) - (r)[k_5(K) + k'_5(K')] - k_6(\mathrm{PO_2})(r)$$

$$\frac{d(K)}{dt} = \frac{k_4}{k_4 + k'_4}\cdot k_2(\mathrm{PO_2}) - k_5(K)(r) - k_7I_0(K)$$

$$\frac{d(K')}{dt} = \frac{k'_4}{k_4 + k'_4}\cdot k_2(\mathrm{PO_2}) - k'_5(K')(r)$$

$$\frac{d(\mathrm{O_2})}{dt} = (k_1 + 2k_2)(\mathrm{PO_2}) + k_3(r) - k_6(\mathrm{PO_2})(r) + 2k_7I_0(K),$$

where I_0 is the intensity of the light. The differential equation for the scissions S of macromolecules is not included because the measurement of oxygen consumption is much more exact than the measurement of scissions.

As the most part of existing experimental data consists of kinetic curves for the consumption of oxygen relative to different modes of photooxidation at different I_0 in stationary conditions, the system of differential equations should be considered with the corresponding system of algebraic equations:

$$-(k_2 + k'_2)(\mathrm{PO_2})_{st} + k_3(r)_{st} + (r)_{st}[k_5(K)_{st} + k'_5(K')_{st}] - k_6(\mathrm{PO_2})_{st}(r)_{st} + 2k_7I_0(K)_{st} = 0$$

$$(k_2 + k'_2)(\mathrm{PO_2})_{st} - k_3(r)_{st} - (r)_{st}[k_5(K)_{st} + k'_5(K')_{st}] - k_6(\mathrm{PO_2})_{st}(r)_{st} = 0$$

$$\alpha\cdot k_2(\mathrm{PO_2})_{st} - k_5(r)_{st}(K)_{st} - k_7I_0(K)_{st} = 0$$

$$(I - \alpha)k_2(\mathrm{PO_2})_{st} - k'_5(r)_{st}(K')_{st} = 0$$

$$(k_1 + 2k_2)(\mathrm{PO_2})_{st} + k_3(r)_{st} - k_6(r)_{st}(\mathrm{PO_2})_{st} + 2k_7I_0(K)_{st} = W_{st},$$

where $\alpha = k_4/(k_4 + k_4')$ and W_{st} is the stationary rate of oxygen consumption.

This system of 5 equations has at every I_0 six unknown values: $k_5(K)$, $k_5'(K')$, $k_7(K)$, α, (PO_2) and (r). The other rate constants were determined earlier.[1] Some of these unknown values are defined directly:

$$(PO_2) = \frac{k_3}{k_6}\cdot\frac{k_1 + 2k_2 + k_2'}{2k_2'}\cdot\left[-1 + \sqrt{1 + \frac{4k_2'W}{(k_1 + 2k_2 + k_2')^2}\cdot\frac{k_6}{k_3}}\right] \tag{1}$$

$$(r) = \frac{k_2'}{k_3}\cdot(PO_2) \tag{2}$$

$$k_7(K) = \frac{k_6}{k_3}\cdot\frac{k_2(PO_2)^2}{I_0} \tag{3}$$

The others are connected by the equations:

$$k_5'(K') = \frac{k_2k_3(I - \alpha)}{k_2'} \tag{4}$$

$$k_5(K) = \frac{k_3k_6}{4k_2'}\cdot\frac{k_7}{k_5}\cdot I_0\left[-1 + \sqrt{1 + \frac{4k_2'}{k_6}\cdot\frac{k_5}{k_7}\cdot\frac{\alpha}{I_0}}\right]^2 \tag{5}$$

$$(PO_2) = \frac{k_3}{2k_2'}\cdot\frac{k_7}{k_5}\cdot I_0\left[-1 + \sqrt{1 + \frac{4k_2'}{k_6}\cdot\frac{k_5}{k_7}\cdot\frac{\alpha}{I_0}}\right] \tag{6}$$

$$\frac{(PO_2)^2}{I_0} = \frac{k_7}{k_5}\cdot\frac{k_2k_3^2}{k_2'^2k_6} - \frac{k_7}{k_5}\cdot\frac{k_3}{k_2'}\cdot(PO_2) \tag{7}$$

(For brevity we have discarded the subscript *st* in Equations 1–7).

This system has an infinite set of solutions for every value of I_0. Yet, if the suggested scheme has a physical sense, i.e., the experimentally known dependence

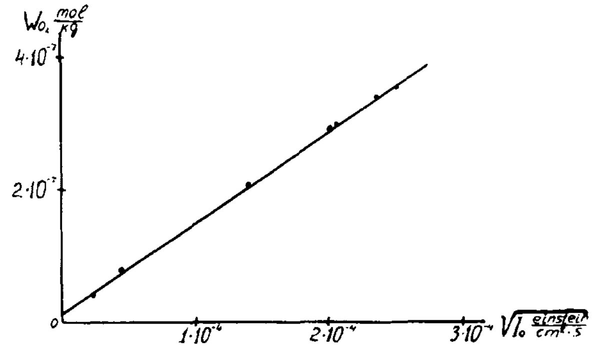


FIGURE 1 Dependence of the stationary rate of the oxygen consumption $(W_{O_2})_{st}$ on the light intensity at wavelengths 365–440 nm.

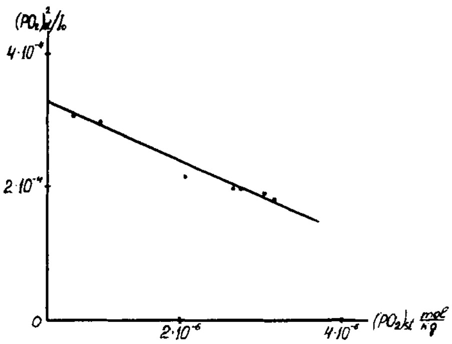


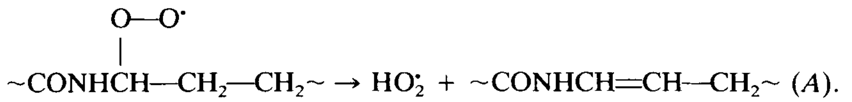
FIGURE 2 The representation of the experimental data of Figure 1 in the coordinates of Equation (7):

$$\frac{(\mathrm{PO}_2)_{st}}{I_0} = \frac{k_7}{k_5}\cdot\frac{k_2K_3^2}{k_2'^2k_6} - \frac{k_7}{k_5}\frac{k_3}{k_2'}(\mathrm{PO}_2)_{st}.$$

of W on I_0 (Figure 1) then a linear dependence of the coordinates of Equation 7 is observed. The latter defines the numerical values of α and k_7/k_5 and so gives a unique solution for the system being considered.

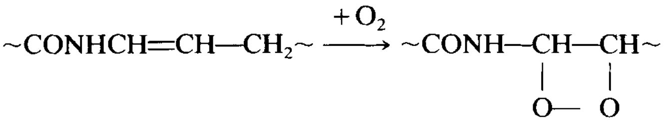
Such a linear dependence really does exist (Figure 2) and gives the values $\alpha = 0.49$ and $k_7/k_5 = 0.029$ with a correlation coefficient 0.98. It is allowed to consider $\alpha = 0.5$ which means that the products K and K' are formed from A in equal quantities and that their stationary concentrations can differ only as a result of subsequent reactions.

We suppose that the intermediate product A is an enamide which is formed as a result of the elimination of radical $\mathrm{HO}_2^\bullet$ from the peroxide macroradical PO_2:

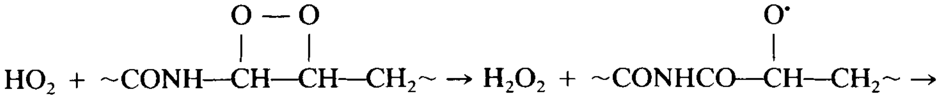


$$\sim\mathrm{CONH}\overset{\mathrm{O{-}O^\bullet}}{\overset{|}{\mathrm{CH}}}\mathrm{{-}CH_2{-}CH_2}\sim\;\rightarrow\;\mathrm{HO_2^\bullet} + \sim\mathrm{CONHCH{=}CH{-}CH_2}\sim\ (A).$$

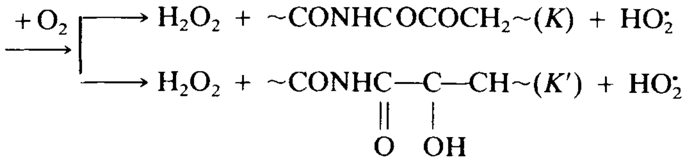
It is known[5–7] that aliphatic enamines and enamides are very easily oxidized in air. The details of this process have been poorly studied, but among the main products are ketoimides and unsaturated ketones which were also found during the photooxidation of PA.[8] So, this part of the mechanism we describe conditionally, through the parallel formation of the ketoimide K and its chemical isomer K':



$$\sim\mathrm{CONHCH{=}CH{-}CH_2}\sim\;\xrightarrow{+\mathrm{O_2}}\;\sim\mathrm{CONH{-}}\underset{\mathrm{O}{-}}{\underset{|}{\mathrm{CH}}}\mathrm{{-}}\underset{\mathrm{O}}{\underset{|}{\mathrm{CH}}}\sim$$



$$\mathrm{HO_2} + \sim\mathrm{CONH{-}}\overset{\mathrm{O}\,-}{\overset{|}{\mathrm{CH}}}\mathrm{{-}}\overset{\mathrm{O}}{\overset{|}{\mathrm{CH}}}\mathrm{{-}CH_2}\sim\;\rightarrow\;\mathrm{H_2O_2} + \sim\mathrm{CONHCO{-}}\overset{\mathrm{O^\bullet}}{\overset{|}{\mathrm{CH}}}\mathrm{{-}CH_2}\sim\;\rightarrow$$



$$\xrightarrow{+O_2} \begin{cases} H_2O_2 + \sim CONHCOCOCH_2\sim (K) + HO_2^{\bullet} \\ H_2O_2 + \sim CONHC(=O)\text{—}C(OH)\text{—}CH\sim (K') + HO_2^{\bullet} \end{cases}$$

It is supposed, and it agrees with Allen's[8] opinion that light of 365 nm photolyses mainly the ketoimide K, but light of 313 nm photolyses its isomer K'.

The next reactions of K and K' with radicals $HO_2^{\bullet}$ are analogous with the known[7] radical splitting of α-diketones and ensure the chain transfer with the scission of a macromolecule, for example, as

$$\sim CONHCOCOCH_2\sim + HO_2^{\bullet} \rightarrow \sim CONHCHO + O_2 + O{=}\dot{C}\text{—}CH_2\sim$$

$$O{=}\dot{C}\text{—}CH_2\sim \xrightarrow{+O_2+PA} O{=}CH\text{—}CH_2\sim + PO_2^{\bullet}.$$

All these notations are very detailed only for the sake of illustration.

It is clear that Equations (1)–(7) do not allow for the possibility of determining the absolute values of the rate constants k_5, k_7 or of the concentration $(K)_{st}$. To achieve this, the full system of differential equations must be solved. The corresponding experimental data, describing the approach of the relative concentration (K) to its stationary value $(K)_{st}$, were discussed in Reference 3. However, the simplified scheme (as it is now known) was used without the participation of the intermediate product K'. Therefore the reliability of the quasi-stationary approximation used in Reference 3 also was not evaluated.

As for the solution of the given system of differential equations, the set of initial conditions is not complete ($(K)_0$ and $(K')_0$ are unknown, and the task is not reduced to Kochi's problem), these conditions must be fit. As the beginning of this fitting may be arbitrary, it is natural to begin with a proof of the reliability of the quasi-stationary approximation.

In this approach we can see:

$$\frac{d(PO_2)}{dt} = 0; \quad \frac{d(r)}{dt} = 0; \quad \frac{d(K)}{dt} = \alpha k_2(PO_2) - k_5(r)(K) - k_7 I_0(K);$$

$$\frac{d(K')}{dt} = (I - \alpha)k_2(PO_2) - k_5'(r)(K') \qquad (\alpha = 0.5)$$

The unknown values are connected also by equations:

$$k_7(K)I_0 = k_6(PO_2)(r); \qquad (r) = \frac{k_2'}{k_3}(PO_2); \qquad k_7(K)I_0 = k_2'\frac{k_6}{k_3}(PO_2)^2.$$

Consequently it can be written:

$$\frac{d(K)}{dt} = \alpha k_2 \sqrt{\frac{k_7(K)I_0}{k_2'} \cdot \frac{k_3}{k_6}} - \frac{k_2'}{k_3} \sqrt{\frac{k_7(K)I_0}{k_2'} \cdot \frac{k_3}{k_6}} \cdot k_5(K) - k_7(K)I_0 \tag{8}$$

$$\frac{d(K')}{dt} = (I - \alpha)k_2 \sqrt{\frac{k_7(K)I_0}{k_2'} \cdot \frac{k_3}{k_6}} - \frac{k_2'}{k_3} \sqrt{\frac{k_7(K)I_0}{k_2'} \cdot \frac{k_3}{k_6}} \cdot k_5'(K') \tag{9}$$

Both these equations integrate in quadratures. It is important to note that in the quasi-stationary approximation (K) does not depend on (K').

The solution of Equation (8) is:

$$\ln\left|\frac{\sqrt{(K)} - \sqrt{(K)_{st}}}{\sqrt{(K)} + \sqrt{(K)_{st}}}\right| = \ln\left|\frac{\sqrt{(K)_0} - \sqrt{(K)_{st}}}{\sqrt{(K)_0} - \sqrt{(K)_{st}}}\right| - \frac{b^2 - 4ac}{2} k_5 t, \tag{10}$$

where

$$a = \frac{k_2'}{k_3} \sqrt{\frac{k_3}{k_2' k_6} \cdot \frac{k_7}{k_5}}; \qquad b = \frac{k_7}{k_5} \cdot I_0; \qquad c = -k_2 I_0 \sqrt{\frac{k_3}{k_2' k_6} \frac{k_7}{k_5}}.$$

It can be written in a short form:

$$\ln\left|\frac{\sqrt{(K)} - \sqrt{(K)_{st}}}{\sqrt{(K)} + \sqrt{(K)_{st}}}\right| = F + Gt \tag{11}$$

with understandable meanings of F and G.
Or

$$(K) = (K)_{st} \left(\frac{I + e^{F+Gt}}{I - e^{F+Gt}}\right)^2 = (K)_{st} \left(\operatorname{cth} \frac{F + Gt}{2}\right)^2 \tag{12}$$

After the substitution of (12) into (9) we can have:

$$\frac{d(K')}{dt} = (I - \alpha)k_2 \sqrt{\frac{k_3}{k_6} \frac{k_7 I_0}{k_2} (K)_{st}} \cdot \operatorname{cth} \frac{F + Gt}{2} \left[I - \frac{k_2'}{(I - \alpha)k_2 k_3} k_5'(K')\right] \tag{13}$$

Or

$$\frac{d(K')}{I - \dfrac{k_2'}{(I - \alpha)k_2 k_3} k_5'(K')} = (I - \alpha)k_2 \sqrt{\frac{k_3}{k_6} \frac{k_7 I_0}{k_2} (K)_{st}} \cdot \operatorname{cth} \frac{F + Gt}{2} dt \tag{14}$$

By setting $t = 0$ $(K') = (K)_0$ after integration (14) we have:

$$\frac{(K')_{st} - (K')}{(K')_{st} - (K')_0} = \left(\frac{\operatorname{sh} \frac{F + Gt}{2}}{\operatorname{sh} \frac{F}{2}} \right)^{\frac{2BC}{G} k'_5} \tag{15}$$

where

$$B = (I - \alpha) k_2 \sqrt{\frac{k_3}{k_6} \frac{k_7 I_0}{k_2}} (K)_{st}$$

and

$$C = \frac{k'_2}{(I - \alpha) k_2 k_3}.$$

After the substitution, for convenience, $A = 2BC$ we redescribe (15) as

$$\frac{(K')_{st} - (K')}{(K')_{st} - (K')_0} = \left(\frac{\operatorname{sh} \frac{F + Gt}{2}}{\operatorname{sh} \frac{F}{2}} \right)^{\frac{A}{G} k'_5} \tag{16}$$

where

$$A = \frac{2k'_2}{k_3} \sqrt{\frac{k_3}{k_6} \frac{k_7 I_0}{k_2}} (K)_{st}$$

Remember that it follows from Equation (4) that $k'_5 (K')_{st} = 20.22\ s^{-1}$. Collecting together the expressions for (K) and (K') in the quasi-stationary approximation and the meanings of the parameters gives:

$$(K) = (K)_{st} \cdot \left(\operatorname{cth} \frac{F + Gt}{2} \right)^2 \tag{12}$$

$$(K') = (K')_{st} - [(K')_{st} - (K')_0]\left(\frac{\operatorname{sh}\dfrac{F+Gt}{2}}{\operatorname{sh}\dfrac{F}{2}}\right)^{\frac{A}{G}k_5'}$$

$$F = \ln\left|\frac{\sqrt{(K)_0} - \sqrt{(K)_{st}}}{\sqrt{(K)_0} + \sqrt{(K)_{st}}}\right| = \ln\left|\frac{\sqrt{k_5(K)_0} - \sqrt{k_5(K)_{st}}}{\sqrt{k_5(K)_0} + \sqrt{k_5(K)_{st}}}\right| \qquad (17)$$

$$G = -\sqrt{\frac{k_7}{k_5}I_0\left(\frac{k_7}{k_5}I_0 + \frac{4k_2}{k_6}\right)\cdot\frac{k_5}{2}}$$

$$A = \frac{2k_2'}{k_3}\sqrt{\frac{k_3}{k_6}\frac{k_7I_0}{k_2}}(K)_{st}$$

Supposing the reliability of the quasi-stationary approximation, the values of $(K)_0$ and k_5 may be evaluated from the representation of the experimental data in the coordinates of Equation (11). Figure 3 shows that the results which were obtained at two different light intensities $I_0 = 6.4 \times 10^{-8}$ and 1.0×10^{-8} einstein/cm$^2\cdot$s are really described by straight lines with a good correlation coefficient (0.97). From the slopes of these lines the rate constant $k_5 = 14260 \pm 5\%$ kg/mol·s is found. The values of $(K)_0$ in these two sets of the experiments were different, and they were evaluated as $(K)_0 = 1.28.10^{-3}$ and $(K)_0 = 1.95.10^{-3}$ mol/kg, respectively.

For the preliminary evaluation of k_5' such a method is not suitable because there is no experimental data which could directly characterize the concentration (K'). Equation (17) shows that at every given value of k_5' a definite dependence between (K') and $(K')_0$ may exist. So at present it is possible only to evaluate the region of real values of k_5'.

The reasonable supposition is that the values of k_5 and k_5' are close to each other

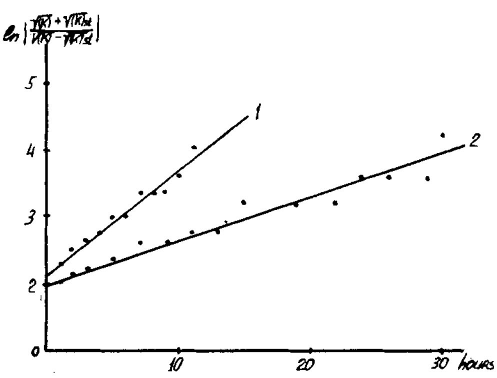


FIGURE 3 Kinetics of the approach of the concentration (K) to its stationary value $(K)_{st}$ in the coordinates of Equation (11): (1) at $I_0 = 6.4 \times 10^{-8}$ einstein/cm$^2\cdot$s; (2) at $I_0 = 1.0 \times 10^{-8}$ einstein/cm$^2\cdot$s

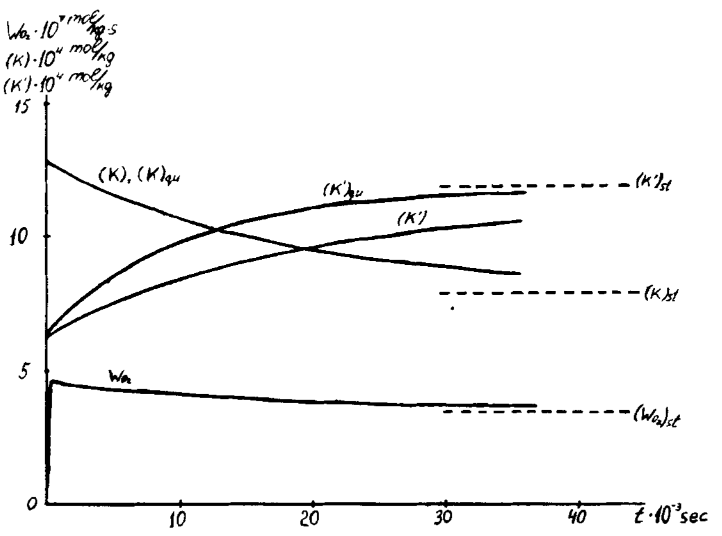


FIGURE 4 Kinetic curves of changes in the rate W_{O_2} and in the concentrations (K) and (K') under the action of light at I_0 6.4 × 10^{-8} einstein/cm^2·s. The curves were calculated exactly [W_{O_2}, (K), (K')] and for the quasi-stationary approximation [$(K)_{qu}$, $(K')_{qu}$].

as are the rate constants of very similar reactions. In this supposition we take the arbitrary but close to k_5 = 14260 kg/mol·s value of k_5', and compare the exact solution of the selected system of differential equations with its solution in the quasi-stationary approximation.

Figure 4 gives an example of such a comparison. Here the kinetic curves of changes in W_{O_2} and the concentrations (K), (K') are represented at I_0 = 6.4 × 10^{-8} einstein/cm^2·s and at an arbitrary value of k_5 = 1.7.10^4 kg/mol·s (which is close to value of k_5). The system of differential equations was solved at the initial conditions: of t = 0 $(PO_2^{\cdot})_0$ = 0, $(r^{\cdot})_0$ = 0, $(K)_0$ = 1.278.10^{-3} mol/kg, $(K')_0$ = 6.322.10^{-4} mol/kg, $(O_2)_0$ = 0 (the value of $(K')_0$ was fitted). Represented also are the kinetic curves for $(K)_{qu}$ and $(K')_{qu}$ which were calculated from Equations (12) and (17). As it is seen that, in the range studied, the kinetic curves for (K) and $(K)_{qu}$ are indistinguishable, but the kinetic curves for (K') and $(K')_{qu}$ are easily distinguished, though all of them smoothly approach stationary values. In this case the maximum difference between (K') and $(K')_{qu}$ reaches 17% of the absolute value, but such a difference has practically no influence on the kinetic curves for (K).

CONCLUSION

More detailed analysis of these patterns requires more complete calculations. At this time it is possible to say that, if the distinction between k_5 and k_5' is no more than one order of magnitude (by the general sense of the chemical mechanism suggested), then the results of the exact calculation and of the calculation in the quasi-stationary approximation of kinetic curves for (K) are practically the same and fully agree with the experimental data. For this condition, the use of the quasi-stationary approximation to describe the kinetic behaviour of the most important intermediate products as simple hyperbolic functions, is fully justified. As the permitted arbitrariness in the choice of the value k'_5 is connected with the same (within limits of one order of magnitude) arbitrariness in the evaluation of the concentration (K'), it gives the scheme enough "flexibility" and inspires more confidence in it. Of course, this does not remove the necessity of carrying out special experiments to study the behaviour of the intermediate product K'.

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