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INDUSTRIAL PHOTOCHEMISTRY
IV: INFLUENCE OF ADDITIVES ON THE SELECTIVITY OF SUCCESSIVE PHOTOCHEMICAL REACTIONS

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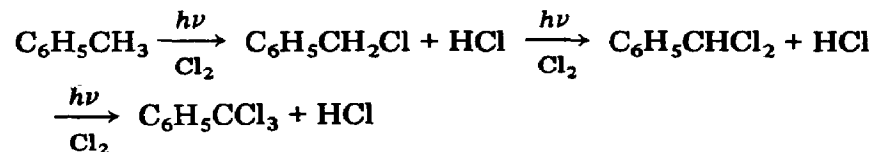
Summary

The selectivity of consecutive photochlorination reactions does not appear to be increased appreciably when the macroscopic factors which govern the working of a photochemical reactor are modified. In the case of toluene and its chlorinated derivatives, we show that in theory it is possible to use additives to orient the photochlorination steps selectively towards the formation of benzyl chloride. However, at present the formation of secondary products perturbing the kinetics limits the potential interest of the use of additives such as phenol or di-*tert*-butylhydroxytoluene.

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1. Introduction

The photochlorination of toluene ($C_6H_5CH_3$) from molecular chlorine can be schematically represented by the following three consecutive chain reactions [1 - 3]:

$$C_6H_5CH_3 \xrightarrow[Cl_2]{h\nu} C_6H_5CH_2Cl + HCl \xrightarrow[Cl_2]{h\nu} C_6H_5CHCl_2 + HCl$$

$$\xrightarrow[Cl_2]{h\nu} C_6H_5CCl_3 + HCl$$

After a given reaction time a mixture of these four products which is a function of the quantity of chlorine which has reacted is produced (Fig. 1). At the same time toluene and its chlorinated derivatives in the chain can undergo chlorination reactions on the ring [4, 5] either by electrophilic substitution or by photochemical addition. These reactions are similar to the polycondensation reactions which lead to the formation of resins [6].
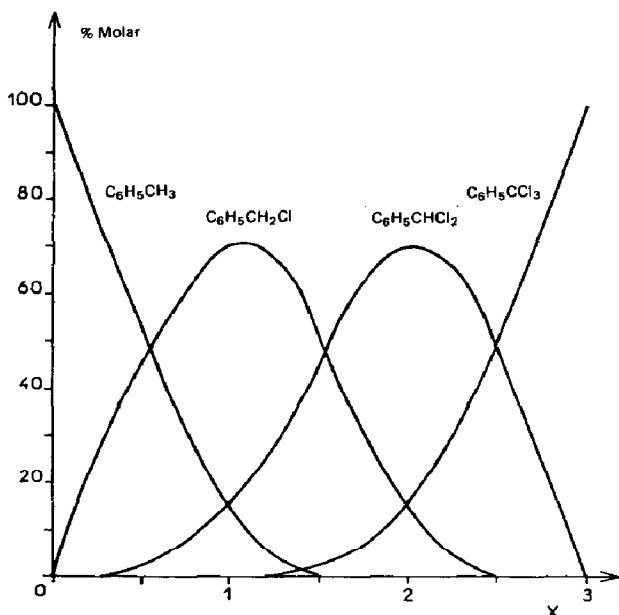
Fig. 1. Production of the mixture of toluene and its chlorinated derivatives on the chain as a function of the extent x of chlorination. The measurements were performed in the kinetic regime at a temperature of 50 °C and an irradiation wavelength of 254 nm.

Since benzyl chloride and phenyl chloroform, which are used as intermediates in organic chemical synthesis, are of greater economic interest than the other primary and secondary derivatives, the industrial application of this synthesis involves a dual problem of selectivity: the optimization of the working conditions of the photoreactor must lead to both the inhibition of secondary reactions and an increase in the selectivity with respect to benzyl chloride and phenyl chloroform. These economic constraints are taken into account by carrying out the industrial photochlorination of toluene in a stirred classical two-phase (gas–liquid) photoreactor and working continuously according to the scheme shown in Fig. 2 which consists of the following stages: toluene is photochlorinated at a temperature of 110 °C and a reasonably low stationary concentration of chlorine up to a degree of chlorination of about 0.5, which corresponds to a concentration of the dichlorinated derivative of the order of 2 vol.%; the non-transformed toluene is separated by distillation and recycled in the reactor; the monochlorinated and dichlorinated derivatives are separated (the latter is produced following a chain of formation of phenyl chloroform).

Substantial economies could be made if the quantity of benzyl chloride produced at a constant degree of chlorination could be increased, *i.e.* if the cost of distillation for the separation of benzylidene chloride could be decreased, all other things being equal. In theory there are two possible approaches to modifying the selectivity of such a reaction: chemical methods in which one or more reagents which are likely to intervene in the mechanism and to favour a particular reaction are added or physical methods in
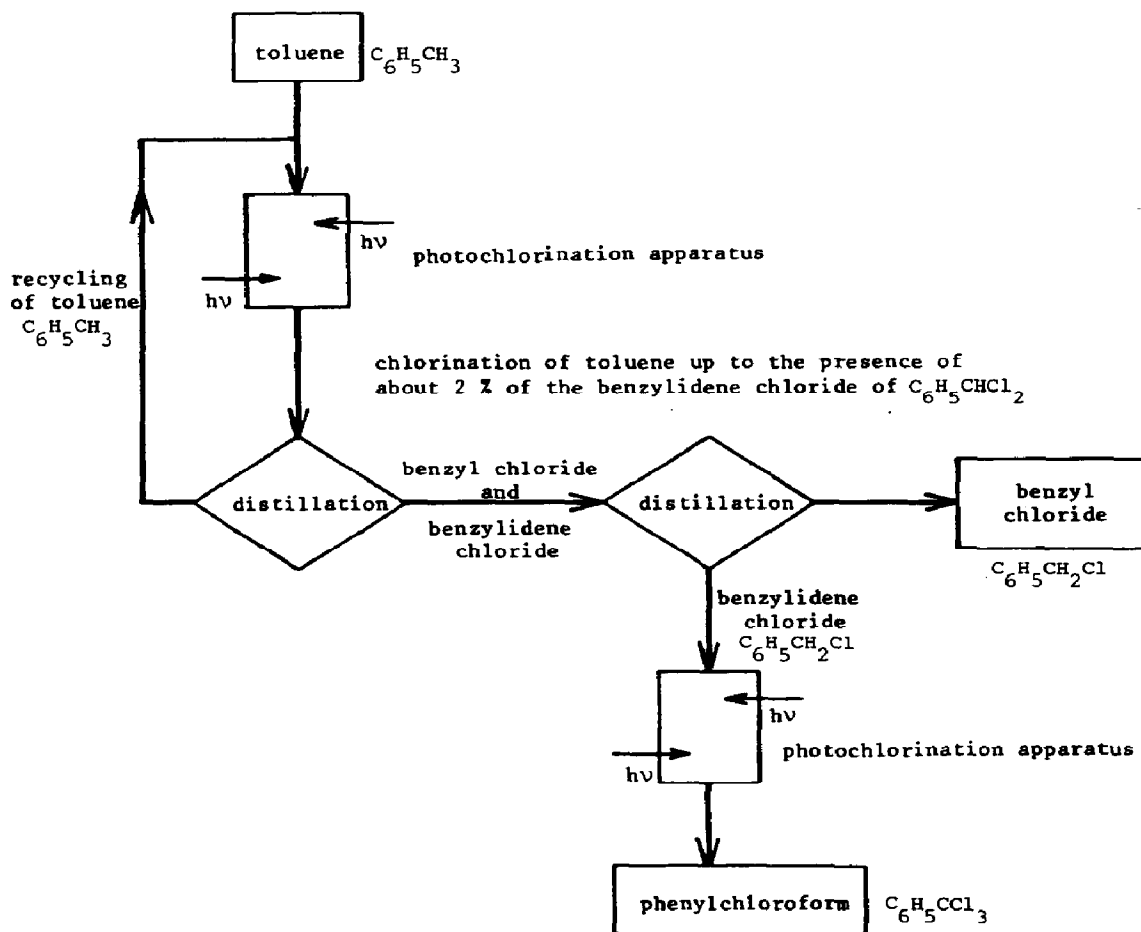
Fig. 2. Schematic diagram of a benzyl chloride production unit.

which the optimal working conditions of the photochemical reactor used for the synthesis are calculated. The latter approach has been considered in the first three parts of this series [7 - 9], and in this paper we report an investigation of a chemical method of improving the selectivity of the photochlorination of toluene. After defining the principles of the method and selecting appropriate additives (mainly phenolic derivatives) we performed a kinetic study of the initial stages of the three chlorination reactions of interest in order to determine their rate constants and a series of tests after the reactions had proceeded for some time in order to determine the feasibility of the process. Although the results obtained during the initial stages of the reaction were promising, the results of the tests at later stages showed that the real gain in selectivity was low and was much less than that predicted. However, although these results show that the process examined here is unsuitable for industrial applications, the principles that we have defined appear to be sufficiently general to encourage further research to determine the ideal additive for increasing the selectivity of both photochemical and non-photochemical consecutive long-chain reactions.

2. Definition of the principles leading to an increase in the selectivity by chemical methods

Figure 3 shows the various radical processes involved in the photochlorination of toluene and its derivatives. The reaction kinetics depend mainly on the concentration of free $Cl^{\bullet}$ atoms [8, 9] and the selectivity is determined by the rate constants of the reactions of $Cl^{\bullet}$ with $C_6H_5CH_3$, $C_6H_5CH_2Cl$ and $C_6H_5CHCl_2$.
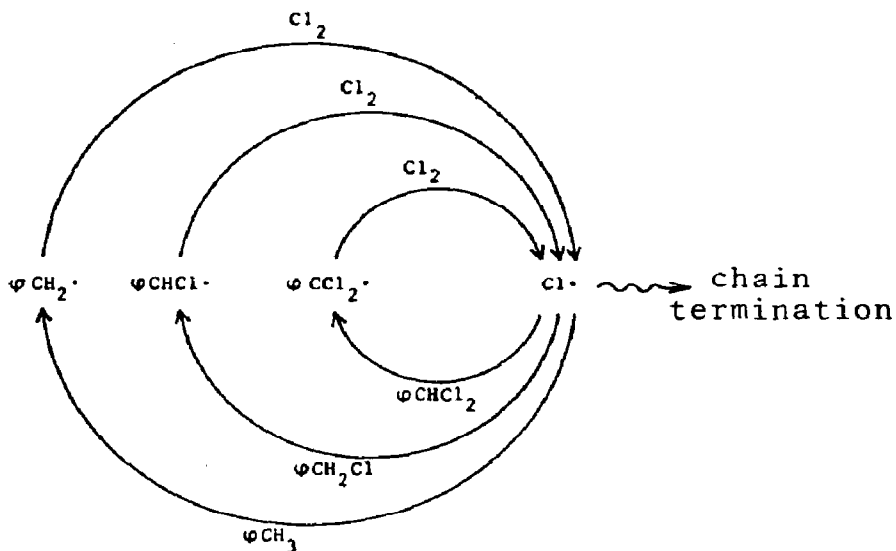

Fig. 3. Schematic diagram of the processes involved in the photochlorination of toluene and its chlorinated derivatives in the chain ($\varphi \equiv C_6H_5$).
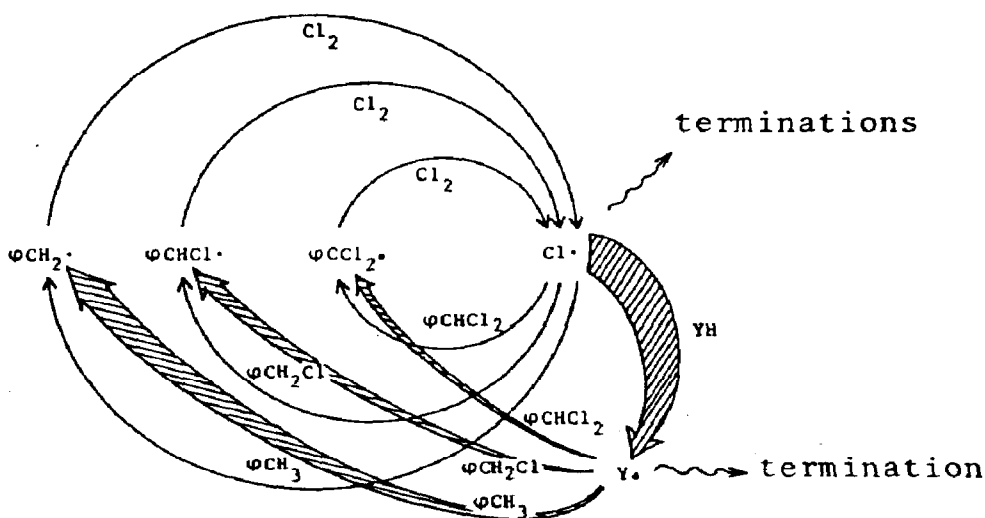

Fig. 4. Schematic diagram of the processes involved in the photochlorination of toluene and its chlorinated derivatives in the chain in the presence of an additive YH ($\varphi \equiv C_6H_5$).

However, if we introduce an additive YH which reacts with $Cl^\cdot$ to form a radical $Y^\cdot$ which does not react with Cl_2 but does react with $C_6H_5CH_3$, $C_6H_5CH_2Cl$ and $C_6H_5CHCl_2$, the selectivity can be modified if the reactivities of this radical with respect to these three compounds are different. As an example Fig. 4 shows the various processes involved in the hypothetical case where the reactivity of $Y^\cdot$ is smaller for higher degrees of chlorination of the toluene derivative. Under these conditions the formation of $C_6H_5CH_2^\cdot$, and hence $C_6H_5CH_2Cl$, is more likely than the formation of $C_6H_5CHCl^\cdot$ or $C_6H_5CCl_2^\cdot$.

3. Initial stages of photochlorination in the presence of YH

In view of the principles discussed in Section 2 the photochlorination mechanism of a compound RH which can be chlorinated in the presence of YH is given by the following scheme: initiation,

$$Cl_2 \xrightarrow{\phi I_a} 2Cl^\cdot \tag{1}$$

propagation (I),

$$Cl^\cdot + RH \xrightarrow{k_2} R^\cdot + HCl \tag{2}$$

$$R^\cdot + Cl_2 \xrightarrow{k_3} Cl^\cdot + RCl \tag{3}$$

propagation (II),

$$Cl^\cdot + YH \xrightarrow{k_4} Y^\cdot + HCl \tag{4}$$

$$RH + Y^\cdot \xrightarrow{k_5} YH + R^\cdot \tag{5}$$

$$RH + Y^\cdot \xleftarrow{k_6} YH + R^\cdot \tag{6}$$

termination,

$$Cl^\cdot + Cl^\cdot \xrightarrow{k_{7a}} \left. \begin{array}{c} \\ \\ \\ \end{array} \right\} \text{ inactive products} \tag{7a}$$

$$Cl^\cdot + Y^\cdot \xrightarrow{k_{7b}} \tag{7b}$$

$$Y^\cdot + Y^\cdot \xrightarrow{k_{7c}} \tag{7c}$$

where RH is a hydrocarbon and YH is an inhibitor.

The following comments can be made about this scheme. In the absence of the inhibitor the mechanism is reduced to the initiation, propagation (I) and termination (reaction 7(a)) steps.

If YH does not absorb the light exciting Cl_2 we assume that the presence of this product does not modify the chain initiation step and therefore the rate of initiation is

$$(V_i)_{RH,YH} = (V_i)_{RH} = \phi I_a$$

The selectivity can only be modified if the stationary concentration of $Cl^\cdot$ atoms decreases. Therefore we have added the two most probable new

termination reactions: recombination of a Cl· atom and a Y· radical, and, at sufficiently large concentrations of Y·, recombination of pairs of these radicals. The principal stoichiometric equation of this mechanism is still

$$RH + Cl_2 = RCl + HCl$$
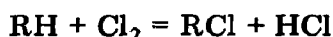
3.1. Calculation of the initial rate of photochlorination

When the chain is assumed to be long and the free radicals are assumed to be in a quasi-stationary state, the initial rate $(V_0)_{RH,YH}$ is given by

$$(V_0)_{RH,YH} = (V_0)_{RH}\left(1 + \frac{k_4}{k_2}\frac{[YH]_0}{[RH]_0}\right) \bigg/ \left\{1 + \frac{k_{7b}}{k_{7a}}\frac{[Y^\cdot]}{[Cl^\cdot]} + \frac{k_{7c}}{k_{7a}}\frac{[Y^\cdot]^2}{[Cl^\cdot]^2}\right\}^{1/2}$$

where

$$\frac{[Y^\cdot]}{[Cl^\cdot]} = \frac{k_4}{k_5}\frac{[YH]_0}{[RH]_0}(1 + \lambda_0)$$

$$\lambda_0 = \frac{k_6}{k_4}\frac{k_2}{k_3}\frac{[RH]_0}{[Cl_2]_0} + \frac{k_6}{k_3}\frac{[YH]_0}{[Cl_2]_0}$$

$$(V_0)_{RH} = k_2\left(\frac{\phi I_a}{k_{7a}}\right)^{1/2}[RH]_0$$

In the absence of YH the most important termination process is the $Cl^\cdot - Cl^\cdot$ recombination reaction which leads to $[R^\cdot]/[Cl^\cdot] \ll 1$, i.e.

$$\frac{[R^\cdot]}{[Cl^\cdot]} = \frac{k_2}{k_3}\frac{[RH]}{[Cl_2]} \ll 1$$

To ensure a substantial modification of the selectivity the hydrogen transfer reactions between the hydrocarbon RH and the Cl· atom must be more rapid than those between RH and the Y· radical, i.e.

$$k_6 < k_4$$

and

$$k_6 < k_3$$

Finally, in order that the proposed method can be applied in practice, the products YH must be able to modify the selectivity at concentrations very much lower than those of the reactants, i.e.

$$[YH]_0 \ll [Cl_2]$$

The preceding inequalities lead to the relation

$$\lambda_0 \ll 1$$

Therefore the expression for the rate $(V_0)_{RH,YH}$ is simplified to

$(V_0)_{RH,YH}$

$$= (V_0)_{RH}\left(1 + \frac{k_4}{k_2}\frac{[YH]_0}{[RH]_0}\right)\bigg/ \left\{1 + \frac{k_{7b}}{k_{7a}}\frac{k_4}{k_5}\frac{[YH]_0}{[RH]_0} + \frac{k_{7c}}{k_{7a}}\left(\frac{k_4}{k_5}\right)^2\frac{[YH]_0^2}{[RH]_0^2}\right\}^{1/2}$$

We can also make the approximation [10]

$$k_{7b} \approx 2(k_{7a}k_{7c})^{1/2}$$

and we finally obtain the analytical expression

$$\frac{(V_0)_{RH,YH}}{(V_0)_{RH}} = \left(1 + \frac{k_4}{k_2}\frac{[YH]_0}{[RH]_0}\right)\bigg/ \left\{1 + \left(\frac{k_{7c}}{k_{7a}}\right)^{1/2}\frac{k_4}{k_5}\frac{[YH]_0}{[RH]_0}\right\}$$

It is therefore appropriate to seek suitable compounds YH and to determine the k_4 values obtained for the chlorination of toluene and its chlorinated derivatives.

3.2. Kinetic studies of the initial stage

When the concentration of free Cl$^\bullet$ atoms in the medium is increased with a consequent increase in the concentration of Y$^\bullet$ radicals, the chain termination processes are favoured; the YH compounds chosen must therefore inhibit the photochlorination of toluene and its chlorinated derivatives.

The best known inhibitors for this type of reaction are oxygen, phenols, amines etc. [11, 12]. However, the mechanisms proposed for the inhibition processes have not been verified experimentally. Consideration of the bond energies of these inhibitors has led us to investigate the influence of phenols (phenol and di-*tert*-butylhydroxytoluene (BHT)) on the initial rate of photochlorination of toluene and its chlorinated derivatives (the energies of the O—H bond of the hydroxyl group of phenol and the C—H bond of the aliphatic chain of toluene are equal (85 kcal mol^{-1})). The Cl$^\bullet$ atom can therefore attack either of these bonds to form the phenoxy or the benzyl radical.

The results reported below show that the phenoxy radical can detach a hydrogen atom from toluene or its chlorinated derivatives and thus regenerate the inhibitor. Therefore another type of chain reaction takes place in the reaction medium which involves the phenoxy radicals but always leads to the same stoichiometric equation:

$$RH + Cl_2 = RCl + HCl$$
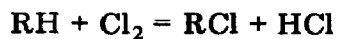
3.2.1. Experimental results

We investigated the effect of the concentration of phenol and BHT on the initial rate of photochlorination of toluene, benzyl chloride and benzylidene chloride. The inhibitor concentrations varied between 10^{-4} and 1.5×10^{-2} mol l^{-1} and the hydrocarbon concentration was 1 mol l^{-1}.

3.2.1.1. Influence of the inhibitor concentration. The ratio $\tau = (V_0)_{\text{RH,YH}}/$ $(V_0)_{\text{RH}}$ (RH $\equiv$ hydrocarbon; YH $\equiv$ inhibitor) of the initial rate of photochlorination in the presence of the inhibitor to that in the absence of the inhibitor was investigated.

Firstly we studied the variations in τ as a function of the molar ratio in the range $0 - 10^{-2}$. The experimental results shown in Figs. 5 and 6 indicate that phenol and BHT are efficient inhibitors of the photochlorination of toluene and its derivatives. For a given value of [YH]/[RH] the efficiency of inhibition varies with the hydrocarbon. For the two inhibitors studied the rate of photochlorination of toluene is the least inhibited. When phenol is the inhibitor the rates of photochlorination of benzyl chloride and benzylidene chloride undergo an identical inhibition effect, whereas when BHT is the inhibitor the photochlorination of benzyl chloride is more strongly inhibited.
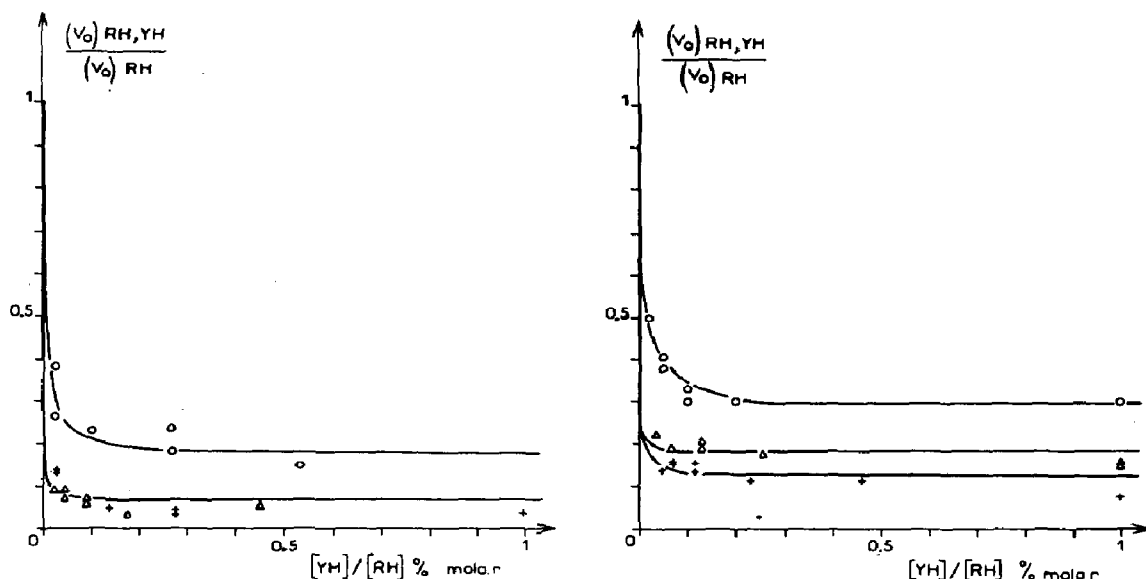

Fig. 5. Photochlorination of toluene (○), benzyl chloride (+) and benzylidene chloride (△) in the presence of phenol: variation in $(V_0)_{\text{RH,YH}}/(V_0)_{\text{RH}}$ as a function of [YH]/[RH] calculated using

$$\frac{(V_0)_{\text{RH,YH}}}{(V_0)_{\text{RH}}} = \left(1 + \frac{k_4}{k_2}\frac{[\text{YH}]_0}{[\text{RH}]_0}\right) \Big/ \left\{1 + \left(\frac{k_{7c}}{k_{7a}}\right)^{1/2}\frac{k_4}{k_5}\frac{[\text{YH}]_0}{[\text{RH}]_0}\right\}$$

Operating conditions: kinetic regime; temperature, 50 °C; solvent, phenyl chloroform; chlorine pressure, 450 Torr. The concentrations and absorbed light intensities are as follows: 10 vol.% toluene, $I_a = 1.9 \times 10^{-11}$ einstein s^{-1} cm^{-3}; 10 vol.% benzyl chloride; $I_a = 0.7 \times 10^{-9}$ einstein s^{-1} cm^{-3}; 10 vol.% benzylidene chloride, $I_a = 0.7 \times 10^{-9}$ einstein s^{-1} cm^{-3}.

Fig. 6. Photochlorination of toluene (○), benzyl chloride (+) and benzylidene chloride (△) in the presence of BHT: variation in $(V_0)_{\text{RH,YH}}/(V_0)_{\text{RH}}$ as a function of [YH]/[RH], calculated as in Fig. 5. The operating conditions are as given in Fig. 5.
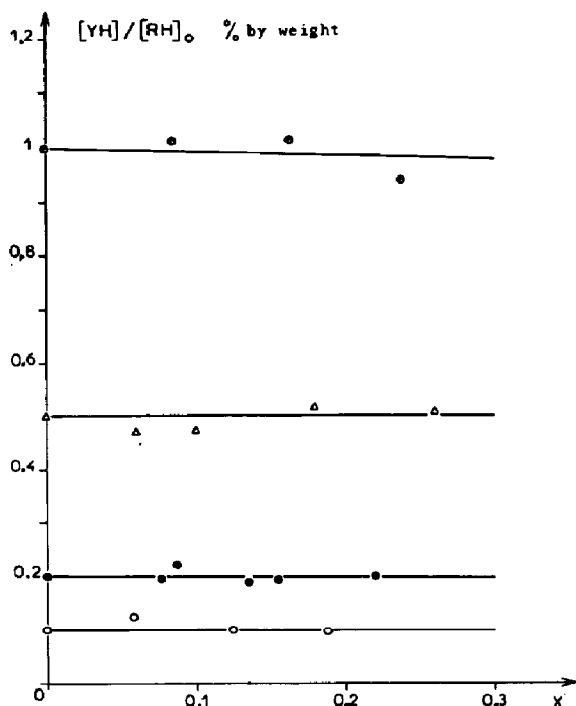
Fig. 7. Demonstration of the lack of consumption of 2,6-dichlorophenol during the photochlorination of toluene: variation in $[YH]/[RH]_0$ with the degree x of chlorination in the kinetic regime at 80 °C and an irradiation wavelength of 313 nm: ——, solvent; ◑, $[YH] = 0.17$ mol l^{-1}; △, $[YH] = 0.083$ mol l^{-1}; ●, $[YH] = 0.33$ mol l^{-1}; ○, $[YH] = 0.017$ mol l^{-1}.

We also found that in the case of toluene some inhibitor was still present for a degree of chlorination of about 0.3 (Fig. 7). In order to permit a more refined chromatographic analysis, this investigation was performed using 2,6-dichlorophenol which is expected to have a reactivity towards toluene and its derivatives comparable with those of BHT and phenol.

3.2.1.2. Influence of the presence of chlorine. In this study the inhibitor concentration was fixed at 10^{-3} mol l^{-1}. Under the operating conditions used here the initial rates of photochlorination in the presence of an inhibitor are independent of the chlorine pressure; these results are shown in Tables 1 and 2.

3.2.1.3. Influence of the absorbed light intensity. This investigation could only be carried out for the chlorination of toluene and benzyl chloride in the presence of BHT at a concentration of 10^{-3} mol l^{-1}. In all other cases, *i.e.* in the photochlorination of benzylidene chloride and when phenol is used as the inhibitor, the rates $(V_0)_{RH,YH}$ were too low to be measured accurately during the attenuation of the absorbed intensity. In the presence of BHT the order of the rate $(V_0)_{RH,YH}$ with respect to the absorbed intensity is always 1/2. These results are shown in Tables 3 and 4.

TABLE 1

Effect of the chlorine pressure on $(V_0)_{RH,YH}$ in the presence of phenol

RH	$(V_0)_{RH,YH}$ ($\times 10^{-7}$ mol s^{-1} cm^{-3}) *at the following pressures*			
	250 Torr	*300 Torr*	*450 Torr*	*500 Torr*
$C_6H_5CH_3$	15	14.5	14	14
$C_6H_5CH_2Cl$	3	2	2.5	2.4
$C_6H_5CHCl_2$	1.5	1.5	1.3	1.2

Operating conditions: temperature, 50 °C; solvent, phenyl chloroform; irradiation wavelength, 313 nm; 10 vol.% toluene, $I_a = 1.9 \times 10^{-11}$ einstein s^{-1} cm^{-3}; 10 vol.% benzyl chloride, $I_a = 0.7 \times 10^{-9}$ einstein s^{-1} cm^{-3}; 10 vol.% benzylidene chloride, $I_a = 0.7 \times 10^{-9}$ einstein s^{-1} cm^{-3}; inhibitor concentration, 10^{-3} mol l^{-1}.

TABLE 2

Effect of the chlorine pressure on $(V_0)_{RH,YH}$ in the presence of a BHT inhibitor

RH	$(V_0)_{RH,YH}$ ($\times 10^{-7}$ mol s^{-1} cm^{-3}) *at the following pressures*			
	250 Torr	*300 Torr*	*450 Torr*	*500 Torr*
$C_6H_5CH_3$	10.5	17.8	18	17.5
$C_6H_5CH_2Cl$	8.5	8	7.5	7.5
$C_6H_5CHCl_2$	5	4.6	4.4	4.4

The operating conditions are as given in Table 1.

TABLE 3

Effect of the absorbed light intensity on toluene (10 vol.%) in the presence of BHT

I_a/I_0	0.75	0.30	0.21
$(V/V_0)_{RH,YH}^2$	0.70	0.34	0.22

Operating conditions: temperature, 50 °C; chlorine pressure, 450 Torr; solvent, phenyl chloroform; irradiation wavelength, 313 nm.

TABLE 4

Effect of the absorbed light intensity on benzyl chloride (10 vol.%) in the presence of BHT

I_a/I_0	0.68	0.32	0.18
$(V/V_0)_{RH,YH}^2$	0.70	0.32	0.17

Operating conditions as in Table 3.

3.2.2. Mechanism of the initial stage

The overall quantum yields of the photochlorination reactions of toluene and its derivatives in the presence of BHT at a concentration of 10^{-3} mol l^{-1} are much greater than unity (Table 5) and these reactions constitute a long-chain mechanism. If the mechanism proposed in Section 3.1 is cor-

TABLE 5

Lengths N of photochlorination chains formed in the presence of BHT

RH	$C_6H_5CH_3$	$C_6H_5CH_2Cl$	$C_6H_5CHCl_2$
N	10^4	6×10^2	10^2

Operating conditions: temperature, 50 °C; chlorine pressure, 450 Torr; solvent, phenyl chloroform; irradiation wavelength, 313 nm; toluene concentration, 10 vol.%; benzyl chloride concentration, 10 vol.%; benzylidene chloride concentration, 40 vol.%; BHT concentration, 10^{-3} mol l^{-1}.

TABLE 6

Rate constant ratios for the BHT inhibitor at 50 °C

	RH		
	$C_6H_5CH_3$	$C_6H_5CH_2Cl$	$C_6H_5CHCl_2$
k_4/k_2	3.1×10^3	20.8×10^3	164×10^3
$\left(\dfrac{k_{7c}}{k_{7a}}\right)^{1/2} \dfrac{k_4}{k_5}$	1.1×10^4	16.6×10^4	88.6×10^4
$\left(\dfrac{k_{7c}}{k_{7a}}\right)^{1/2} \dfrac{k_2}{k_5}$	3.6	8	5.4

rect, the measured rate of the reaction must be proportional to the square root of the absorbed light intensity and independent of the chlorine pressure. This is verified experimentally.

The results presented in Figs. 5 and 6 show that it is possible to adjust the relation

$$\frac{(V_0)_{RH,YH}}{(V_0)_{RH}} = f\left(\frac{[YH]_0}{[RH]_0}\right)$$

to the experimental results by an optimization method and hence the rate constant ratios

$$\frac{k_4}{k_2} \qquad \left(\frac{k_{7c}}{k_{7a}}\right)^{1/2} \frac{k_4}{k_5} \qquad \left(\frac{k_{7c}}{k_{7a}}\right)^{1/2} \frac{k_2}{k_5}$$

can be calculated (see Tables 6 and 7).

If YH is not consumed the observed inhibition of the photochlorination of toluene and its derivatives cannot be interpreted in terms of a process of cochlorination of this inhibitor. The final reaction, which occurs by electrophilic substitution, does not change the concentration of $Cl^{•}$ atoms in the medium and therefore does not modify the rate of photochlorination of the hydrocarbon. The inhibitor effect cannot be explained by a simple chain breaking process of the type

TABLE 7

Rate constant ratios for the phenol inhibitor at 50 °C

	RH		
	$C_6H_5CH_3$	$C_6H_5CH_2Cl$	$C_6H_5CHCl_2$
k_4/k_2	3.8×10^3	26.5×10^3	20.1×10^3
$\left(\dfrac{k_{7c}}{k_{7a}}\right)^{1/2} \dfrac{k_4}{k_5}$	2.2×10^4	36.4×10^4	29×10^4
$\left(\dfrac{k_{7c}}{k_{7a}}\right)^{1/2} \dfrac{k_2}{k_5}$	5.7	14.6	14.4

$$YH + Cl^{\cdot} \xrightarrow{k_4} Y^{\cdot} + HCl \qquad (4)$$

$$Cl^{\cdot} + Y^{\cdot} \xrightarrow{k_{7b}} YCl \qquad (7b)$$

$$Y^{\cdot} + Y^{\cdot} \xrightarrow{k_{7c}} Y-Y \qquad (7c)$$

In this model the expression for the ratio of the rates is

$$\frac{(V_0)_{RH,YH}}{(V_0)_{RH}} = (2\phi I_a)^{1/2} \frac{k_{7a}}{k_4} \frac{1}{[YH]_0}$$

$(V_0)_{RH,YH}$ would thus be proportional to the absorbed intensity which does not agree with experiment.

Only the addition of processes (5) and (6) to process (4) which results in the production of a second propagation chain which consumes all the chlorine allows us to interpret the experimental results.

3.2.2.1. Calculation of the rate constants. By using a value of about 10^2 l mol^{-1} s^{-1} for k_{7c} [10, 13] and the values for k_2 determined in a previous study [14], we obtain values of 10^{11} l mol^{-1} s^{-1} and $10^{10.9}$ l mol^{-1} s^{-1} respectively for the rate constants k_4 with phenol and BHT inhibitors respectively. No published data are available for comparison.

The values obtained for k_4 are, within the limits of experimental error, comparable with the diffusion constant in toluene ($k_D \approx 10^{10}$ l mol^{-1} s^{-1}). Reactions (4) are therefore diffusion limited. We can then deduce the values of the constants k_5 which are shown in Table 8. The results obtained correspond closely to the qualitative description given in Fig. 4, the most interesting YH compound being phenol. The results obtained in the initial stages of the reaction therefore allow us to propose theoretical chemical pathways for improving the selectivity of the photochlorination of toluene.

TABLE 8

Values of k_5 $(l\ mol^{-1}\ s^{-1})$ at 50 °C

Inhibitor	log k_5 for the following compounds		
	$C_6H_5CH_3$	$C_6H_5CH_2Cl$	$C_6H_5CHCl_2$
Phenol	5.3	4.0	3.1
BHT	5.5	4.3	3.6

4. Applications of the inhibition process to the improvement of selectivity in the continuous formation of benzyl chloride
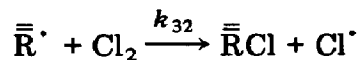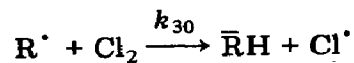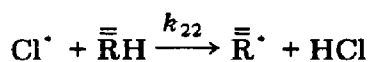
If a constant concentration of inhibitor is maintained in the reactor an increase in the ratio should result in the appearance of an increase in the benzyl chloride concentration and a decrease in the toluene concentration on the product distribution curve (see **Fig. 1**) for a given extent of chlorination.

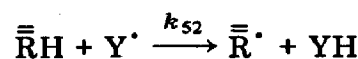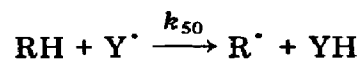### 4.1. Mechanism of the successive chlorination of toluene and its chlorinated derivatives in the presence of YH

The complete mechanism of the photoreaction can be represented as follows: initiation,

$$Cl_2 \xrightarrow[\phi I_a]{h\nu} 2Cl^\bullet \tag{1}$$

propagations,

$$Cl^\bullet + RH \xrightarrow{k_{20}} R^\bullet + HCl$$

$$Cl^\bullet + \bar{R}H \xrightarrow{k_{21}} \bar{R}^\bullet + HCl \tag{2}$$

$$Cl^\bullet + \bar{\bar{R}}H \xrightarrow{k_{22}} \bar{\bar{R}}^\bullet + HCl$$

$$R^\bullet + Cl_2 \xrightarrow{k_{30}} \bar{R}H + Cl^\bullet$$

$$\bar{R}^\bullet + Cl_2 \xrightarrow{k_{31}} \bar{\bar{R}}H + Cl^\bullet \tag{3}$$

$$\bar{\bar{R}}^\bullet + Cl_2 \xrightarrow{k_{32}} \bar{\bar{R}}Cl + Cl^\bullet$$

transfers,

$$Cl^\bullet + YH \xrightarrow{k_4} Y^\bullet + HCl \tag{4}$$

$$RH + Y^\bullet \xrightarrow{k_{50}} R^\bullet + YH$$

$$\bar{R}H + Y^\bullet \xrightarrow{k_{51}} \bar{R}^\bullet + YH \tag{5}$$

$$\bar{\bar{R}}H + Y^\bullet \xrightarrow{k_{52}} \bar{\bar{R}}^\bullet + YH$$

terminations,

$$Cl^{\cdot} + Cl^{\cdot} \xrightarrow{k_{7a}} \left. \begin{array}{l} \\ \\ \end{array} \right\} \text{ inactive products}$$ (7a)

$$Cl^{\cdot} + Y^{\cdot} \xrightarrow{k_{7b}}$$ (7b)

$$Y^{\cdot} + Y^{\cdot} \xrightarrow{k_{7c}}$$ (7c)

(RH $\equiv$ toluene, $\bar{R}H \equiv$ benzyl chloride, $\bar{\bar{R}}H \equiv$ benzylidene chloride and $\bar{\bar{R}}Cl \equiv$ phenyl chloroform).

The rate constants of the various processes are important in the determination of the rate under investigation. It is possible to calculate the variations in the concentration of $\bar{R}H$, $\bar{\bar{R}}H$ and $\bar{\bar{R}}Cl$ with time as a function of the YH concentration or to calculate the variation in the distribution of the chlorinated products as a function of the degree of chlorination and the YH concentration which is assumed to be constant in the medium.

4.2. Prediction of the modification of the selectivity in the presence of YH

We used the rate constants calculated in Section 3 and the relation

$$k_{7b} = 2(k_{7a}k_{7c})^{1/2}$$

to determine the following expressions for the rates of formation or disappearance of the various compounds:

$$\frac{d[RH]}{dt} = -k_{30}[R^{\cdot}][Cl_2]$$

$$= -k_{20}[RH][Cl^{\cdot}] - k_{50}[RH][Y^{\cdot}]$$

$$\frac{d[\bar{R}H]}{dt} = -\frac{d[RH]}{dt} - k_{21}[\bar{R}H][Cl^{\cdot}] - k_{51}[\bar{R}H][Y^{\cdot}]$$

$$\frac{d[\bar{\bar{R}}H]}{dt} = -\left(\frac{d[RH]}{dt} + \frac{d[\bar{R}H]}{dt}\right) - k_{22}[\bar{\bar{R}}H][Cl^{\cdot}] - k_{52}[\bar{\bar{R}}H][Y^{\cdot}]$$

where

$$[Cl^{\cdot}]$$

$$= \frac{(\phi I_a)^{1/2}(2k_{7c}^{1/2}[\phi I_a]^{1/2} + k_{50}[RH] + k_{51}[\bar{R}H] + k_{52}[\bar{\bar{R}}H])}{2k_{7a}^{1/2}k_{7c}^{1/2}(\phi I_a)^{1/2} + k_4[YH]k_{7c}^{1/2} + k_{7a}^{1/2}(k_{50}[RH] + k_{51}[\bar{R}H] + k_{52}[\bar{\bar{R}}H])}$$

$$[Y^{\cdot}] = \frac{(\phi I_a)^{1/2}}{k_{7c}^{1/2}} - \left(\frac{k_{7a}}{k_{7c}}\right)^{1/2}[Cl^{\cdot}]$$

Figure 8 shows the variations in the selectivity of the reaction RH $\rightarrow$ $\bar{R}H$ in the presence of 2 vol.% $\bar{R}H$ as a function of [YH] for a perfectly stirred reactor. The calculations were performed by numerical integration
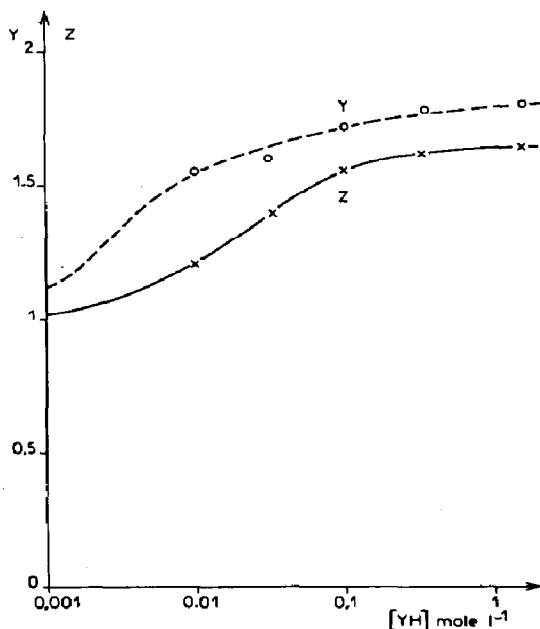
Fig. 8. Variations in the selectivity Z of the photochlorination of toluene with respect to benzyl chloride ($\times$) and in the relative time Y of reaction required to obtain 2 vol.% benzylidene chloride ($\circ$) with the phenol concentration [YH].

for an absorbed intensity such that $\phi I_a \approx 10^{-5}$ einstein l^{-1} s^{-1} using the rate constants determined in this work. This figure shows that a 60% gain in selectivity is theoretically possible. However, the presence of YH results in a marked decrease in the productivity of the process because the length of time spent in the reactor is substantially increased by a factor which could be as high as 60. This problem can be overcome by increasing the number of lamps so that the intensity of the absorbed light is increased. (This modification of the photoreactor must not produce a prohibitive increase in the capital cost of the apparatus.)

4.3. Optimization of the reaction

In the calculations presented above we chose a constant concentration of YH in the medium which resulted in a substantial inhibition of the photochlorination reactions under investigation. Now our interest in using YH is based on the fact that its inhibiting effect on the reaction RH → $\bar{R}$H is less than that on the other reactions and since the concentrations of $\bar{R}$H and $\bar{\bar{R}}$H are negligible at the onset of photochlorination the presence of YH cannot increase the selectivity but only inhibit the photochlorination process. Under these conditions it is possible to propose a simple method consistent with the use of an adapted photoreactor in which the YH concentration could be increased as a function of the extent of photochlorination. This optimization of the reaction enables the irradiation time to be decreased such that the reaction in the presence of YH becomes industrially viable.

4.4. Experimental results

The comment in Section 4.3 suggests that, even if the irradiation time required for the formation of R̄H at R̄H concentrations in the medium of up to 2 vol.% cannot be longer in the absence of YH, it may be economically interesting to attempt to change the selectivity of the reaction and therefore to determine whether the model presented is industrially viable.

The experimental results obtained in a half-closed reactor for different YH concentrations are shown in Figs. 9 - 12. These results show that there is a distinct increase in the selectivity of R̄H at low degrees of chlorination (in practice less than 0.15). At higher degrees of chlorination the quantity of R̄H formed is much higher than the value calculated theoretically.

4.5. Search for the cause of the phenomena

There are two possible reasons for the increase in the relative rate of formation of R̄H with respect to that of RH when the degree of chlorination increases: the disappearance of YH with time; the appearance of accelerators of the formation of R̄H during chlorination (this is the case if a substance ZH is formed where Z˙ is more reactive than Cl˙ with respect to R̄H).
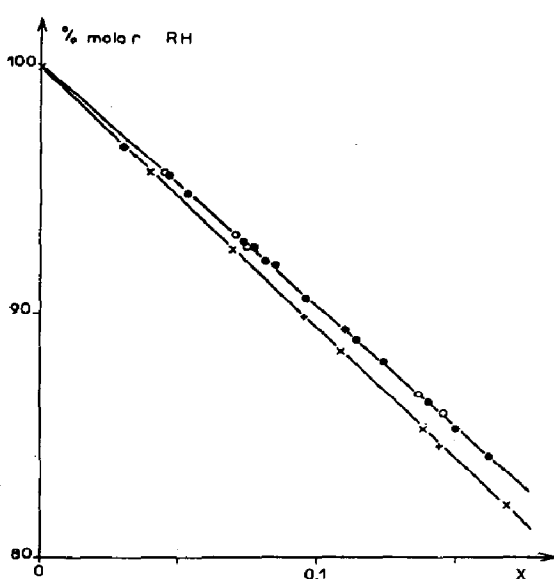

Fig. 9. Variation in [C$_6$H$_5$CH$_3$] with the degree x of chlorination in the absence and the presence of BHT for degrees of chlorination below 0.2: ×, [YH]$_0$ = 0 (theoretical); +, [YH]$_0$ = 0.11 mol l^{-1} (theoretical); ○, [YH]$_0$ = 0 (experimental); ●, [YH]$_0$ = 0.11 mol l^{-1} (experimental); ——, solvent (operating conditions: kinetic regime; temperature, 80 °C; irradiation wavelength, 313 nm).
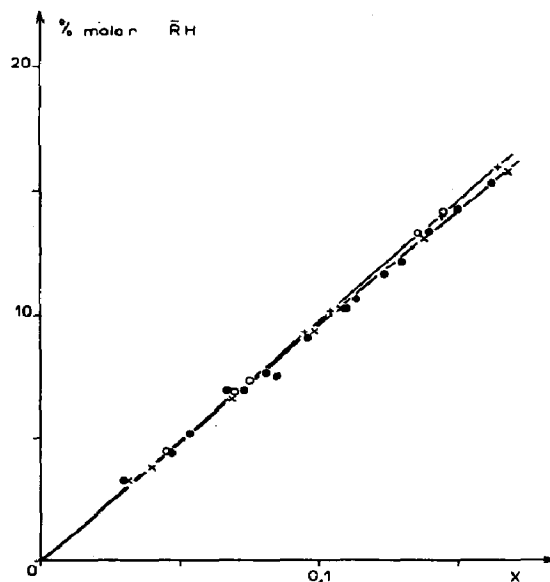
Fig. 10. Variation in [C$_6$H$_5$CH$_2$Cl] with the degree x of chlorination in the absence and the presence of BHT for degrees of chlorination below 0.2: ×, [YH]$_0$ = 0 (theoretical); +, [YH]$_0$ = 0.11 mol l^{-1} (theoretical); ○, [YH]$_0$ = 0 (experimental); ●, [YH]$_0$ = 0.11 mol l^{-1} (experimental); ——, solvent. The operating conditions are as given in Fig. 9.
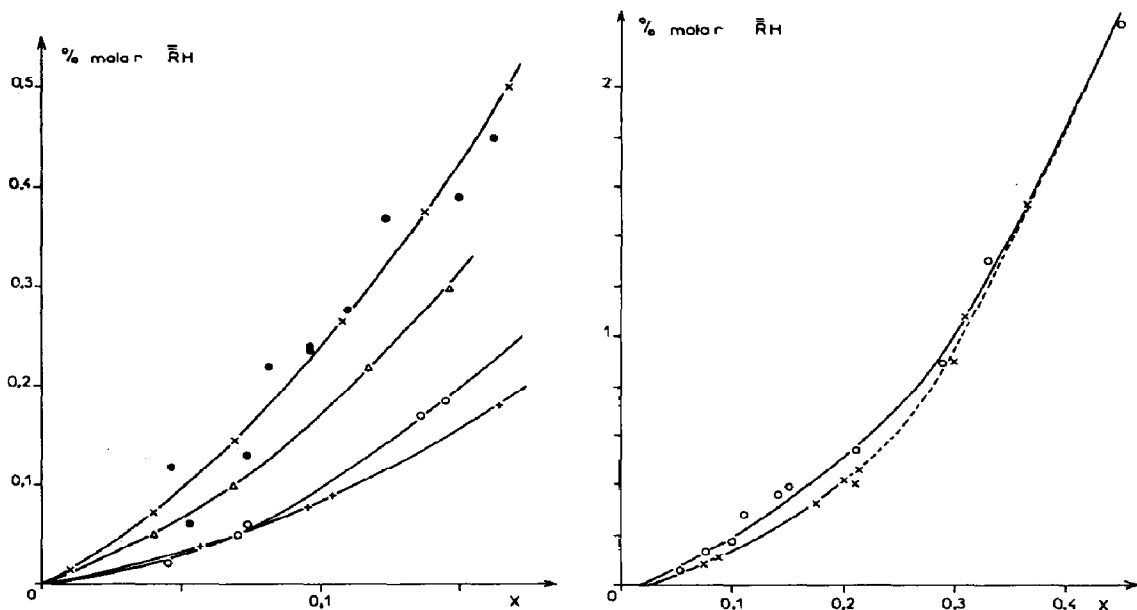
Fig. 11. Variation in [C₆H₅CHCl₂] with the degree *x* of chlorination in the absence and the presence of BHT for degrees of chlorination below 0.2: ×, [YH]₀ = 0 (theoretical); +, [YH]₀ = 0.11 mol l⁻¹ (theoretical); ○, [YH]₀ = 0 (experimental); △, [YH]₀ = 0.01 mol l⁻¹ (experimental); ●, [YH]₀ = 0.11 mol l⁻¹ (experimental); ——, solvent. The operating conditions are as given in Fig. 9.

Fig. 12. Variation in [C₆H₅CHCl₂] with the degree *x* of chlorination in the absence and the presence of BHT for degrees of chlorination below 0.2: ○, [YH]₀ = 0; ×, [YH]₀ = 0.05 mol l⁻¹; ——, solvent. The operating conditions are as given in Fig. 9.

Since the inhibitor is not completely consumed during the photo-chlorination (see Fig. 7), accelerators of the formation of R̄H must be pro-duced. To verify the formation of ZH experimentally we examined mixtures of toluene derivatives corresponding to a given degree x_0 of chlorination and a given YH concentration. It is then possible to compare the relative rates of formation of R̄H and RH for identical degrees x_0 of chlorination in solutions photochlorinated from $x = 0$ to $x = x_0$ and for "new" solutions correspond-ing to x_0. The results of the experiments are shown in Fig. 13 in which the modification of the selectivity, probably because of the presence of a sub-stance formed during chlorination, can clearly be seen.

The accelerator has not been identified because of the large number of primary and secondary products present in the system.

5. Conclusion

The results reported in this paper are completely negative from an industrial viewpoint. However, it appears possible in theory to use chemical methods to modify the selectivity of successive photochemical reactions such as those studied here. The experiments performed here have not con-
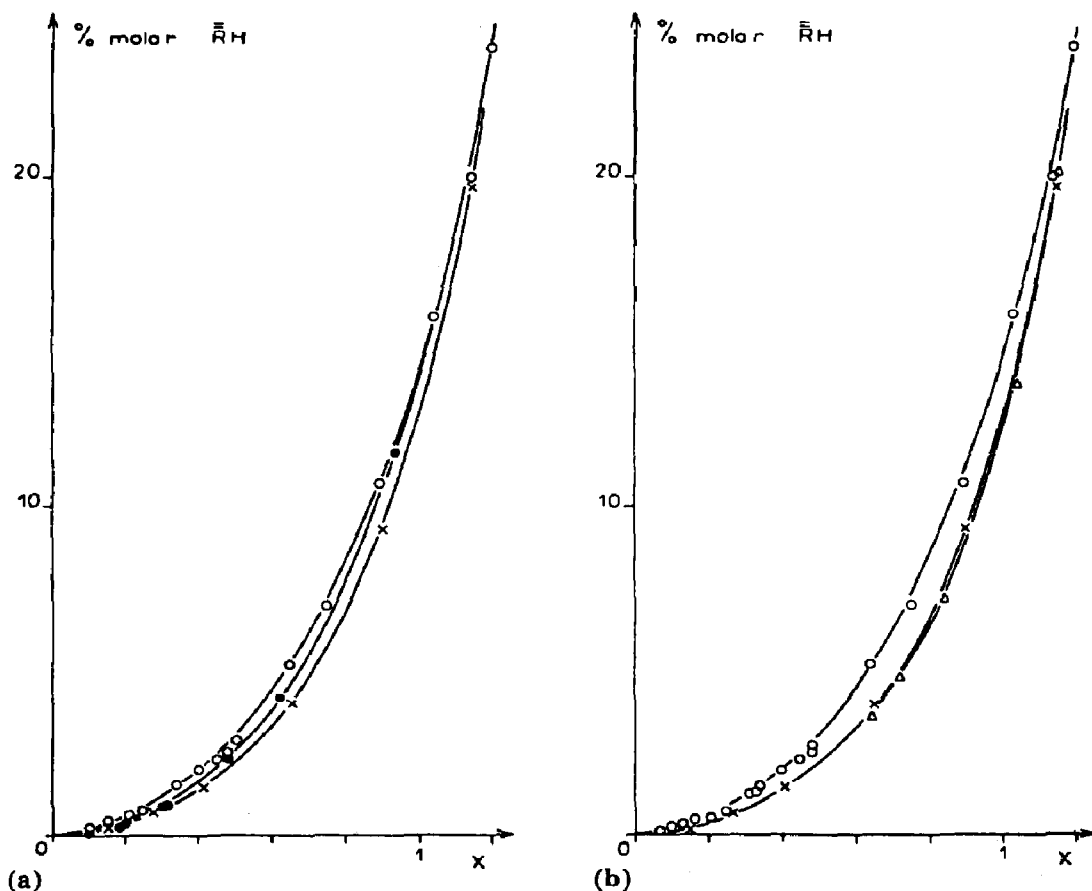
Fig. 13. Variation in [$C_6H_5CHCl_2$] with the degree x of chlorination and the initial reactant concentrations in the absence and the presence of BHT: ———, solvent; ○, [YH]$_0$ = 0, [RH]$_0$ = 9.42 mol l^{-1}, [$\overline{\overline{RH}}$]$_0$ = 0, [$\overline{\overline{RH}}$]$_0$ = 0, x_0 = 0; ●, [YH]$_0$ = 0.11 mol l^{-1}, [RH]$_0$ = 9.42 mol l^{-1}, [$\overline{RH}$]$_0$ = 0, [$\overline{\overline{RH}}$]$_0$ = 0, x_0 = 0; ×, [YH]$_0$ = 0.11 mol l^{-1}, [RH]$_0$ = 8.05 mol l^{-1}, [$\overline{RH}$]$_0$ = 1.24 mol l^{-1}, [$\overline{\overline{RH}}$]$_0$ = 0.016 mol l^{-1}, x_0 = 0.15; △, [YH]$_0$ = 0.11 mol l^{-1}, [RH]$_0$ = 3.72 mol l^{-1}, [$\overline{RH}$]$_0$ = 4.93 mol l^{-1}, [$\overline{\overline{RH}}$]$_0$ = 0.29 mol l^{-1}, x_0 = 0.55.

firmed the theoretical predictions because one or more byproducts formed during the photochlorination accelerate the formation of benzylidene chloride relative to that of benzyl chloride. Further investigations of these chlorination reactions, which form an interesting model, are required in the following domains: a search for alternative additives which will play an identical role with that of the phenolic compounds used in the present work but with a greater efficiency; a search for other types of photoreactors. These investigations will be undertaken in the future.

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