

## KINETICS OF PARTLY DIFFUSION-CONTROLLED REACTIONS XIII: CAGE EFFECT IN THE PHOTOLYSIS OF BENZYL CHLORIDE

A. TOURNIER and X. DEGLISE

*Laboratoire de Photochimie Appliquée, Laboratoire associé au CNRS 328, Ecole Nationale Supérieure des Industries Chimiques, Institut National Polytechnique de Lorraine and University of Nancy I, 1 rue Grandville, 54042 Nancy Cédex (France)*

J. C. ANDRÉ

*Groupe de Recherche et Applications en Photophysique et Photochimie, Laboratoire associé au CNRS 328, Ecole Nationale Supérieure des Industries Chimiques, Institut National Polytechnique de Lorraine and University of Nancy I, 1 rue Grandville, 54042 Nancy Cédex (France)*

(Received June 22, 1982; in revised form October 27, 1982)

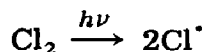
### Summary

The cage recombination of free benzyl and chloride radicals after their formation via the photolysis of benzyl chloride is interpreted using a model of partly diffusion-controlled reactions. A kinetic model is presented which takes into account the non-contact of the species of interest at the moment of their formation. There is good agreement between the experimental results and the model presented. At the same time we show the presence of a secondary cage effect between benzyl radicals and radicals produced by the reaction of  $\text{Cl}^\cdot$  with the solvent.

---

### 1. Introduction

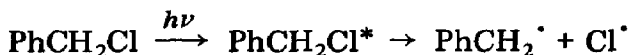
The chain reaction of chlorination of toluene and its derivatives can be initiated by the irradiation of chlorine at 313 nm; the initiation process is then [1]



In order to show the influence that the molar extinction coefficient has on the apparent reaction kinetics of the chlorination of toluene and/or its derivatives, we have irradiated solutions at other wavelengths, in particular at 254 nm. Now, under these irradiation conditions, toluene and its derivatives absorb a large part of the exciting light. In the particular case of benzyl chloride, we investigated the nature of the initiation which could follow the absorption of light by this compound. Most of the experiments were performed in the absence of chlorine in order to avoid all amplification

phenomena related to the existence of chain radical processes which would mask the initiation step.

We were able to demonstrate the formation of the benzyl radical  $\text{PhCH}_2\cdot$  and chloride atoms by the process

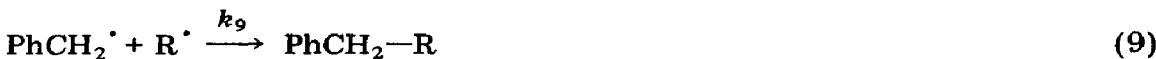
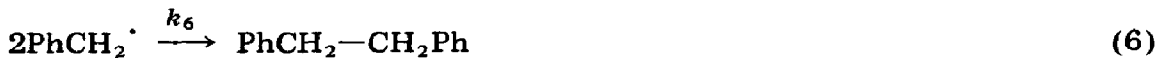
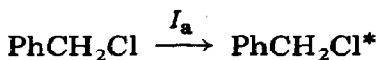


In the absence of a reagent medium (essentially  $\text{Cl}_2$ ), the yield of this reaction depends on the viscosity of the medium and the effect observed has been interpreted using a diffusional "cage" mechanism which is described here.

The results of our calculations show that the quantum yield of initiation of the photochlorination of benzyl chloride can be reasonably represented by the quantum yield of formation of HCl as a result of the photolysis of benzyl chloride.

## 2. The first cage reaction

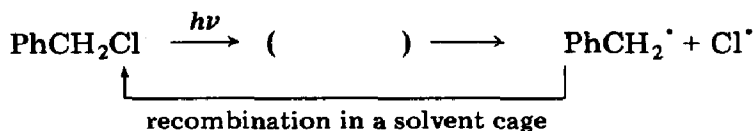
Since kinetic studies [2] have shown that the photolysis of benzyl chloride is a step reaction, we propose the following kinetic scheme for the initial reaction:



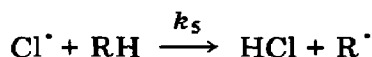
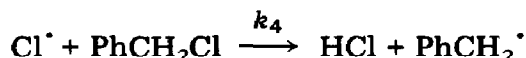


This scheme is similar to that proposed by Hyomaki and Koskikallio [3] for the photolysis of benzyl chloride in a water–methanol mixture. It is also very similar to that proposed by Ichimura and Mori [4] for the gas phase photolysis of a benzyl chloride–butane mixture. Since the medium is non-polar (hydrocarbon solvent), we retain only the radical processes.

The decomposition of  $\text{PhCH}_2\text{Cl}$  occurs by the process



The chlorine atoms thus formed react outside the solvent cage by the two processes



where  $\text{RH}$  represents the hydrocarbon solvent.

Thus, if we assume that the real initiation has a yield close to unity, the measurement of the quantum yield of formation of  $\text{HCl}$  allows us to determine the yield  $\phi_r$  of recombination in the solvent cage because

$$\phi_r = 1 - \phi_{\text{HCl}}$$

Indeed, when the high reactivity of  $\text{Cl}\cdot$  in solution is taken into account, we can neglect (as is also shown by the influence of the absorbed light intensity on the kinetics of the photolysis) the recombination processes of  $\text{Cl}\cdot$  with  $\text{Cl}\cdot$  and with other radicals present outside the cage.

A very simplified kinetic model representing the recombination of two reactive species in a solvent cage has recently been proposed by André *et al.* [5]; in this model it is assumed that at the instant of their formation the two species are located beside each other.

If  $\beta$  represents the ratio of the chemical reaction constant  $k_c$  ( $\text{mol}^{-1} \text{l s}^{-1}$ ) to the diffusion constant  $k_d$ , *i.e.*

$$\beta = k_c/k_d$$

$$k_d = 4\pi N\sigma D$$

where  $\sigma$  is the collision distance,  $N$  is Avogadro's number and  $D$  is the diffusion coefficient of the two species, and if

$$\gamma = \frac{K_2 \sigma^2}{D}$$

where  $K_2$  ( $s^{-1}$ ) is the sum of the rate constants of disappearance of  $Cl^{\cdot}$  and  $PhCH_2^{\cdot}$  ( $K_2 = k_4[PhCH_2Cl] + k_5[RH]$ ), the yield  $\phi_r$  of recombination is approximately expressed by the relation

$$\phi_r = \frac{\beta}{\gamma^{1/2} + \beta + 1}$$

We have assumed that  $\sigma = 6 \text{ \AA}$  and  $D = 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  for the two species when the viscosity is 1 cP and that Stokes' law holds, and we have calculated the best value for the parameter  $\beta$  using a least-squares technique. Since  $k_4 = 4 \times 10^6 \text{ mol}^{-1} \text{ l s}^{-1}$  [6] and  $k_5 = 9.7 \times 10^9 \text{ mol}^{-1} \text{ l s}^{-1}$ , the constant  $k_c$  is of the order of  $2.53 \times 10^9 \text{ mol}^{-1} \text{ l s}^{-1}$ . However, as the results presented in Fig. 1 show, there is only partial agreement between the kinetic model and the experimental data.

Under these conditions, in agreement with the proposals of Noyes [8] for the cage effect, we have assumed that an excess of energy, which is partly kinetic, exists on the formation of the two species and this results in their being separated by a distance greater than the collision distance  $\sigma$ . Therefore the model presented in ref. 5 has to be modified to take this behaviour into account.

In order to calculate the best kinetic parameters by a least-squares method we have developed a simplified kinetic model which takes into account the configurational distribution and the relative diffusion of the

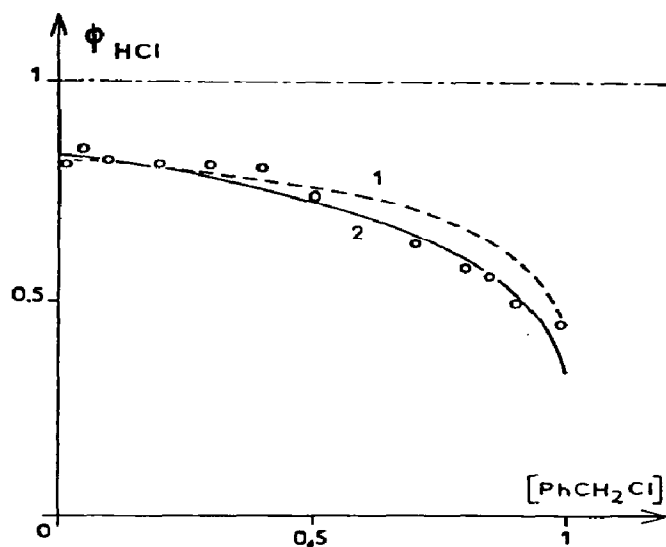


Fig. 1. Variation in  $\phi_{HCl}$  with the volume fraction of benzyl chloride in a benzyl chloride-decane binary mixture at 40 °C: curve 1, calculated from a simplified model [5]; curve 2, calculated from the simplified model presented here.

reactants. Using the nomenclature defined in ref. 5 we solve the following equation which is a function of time and space:

$$\frac{\partial[\text{Cl}^\cdot]}{\partial t} = D \nabla^2[\text{Cl}^\cdot] - K_2[\text{Cl}^\cdot]$$

where  $[\text{Cl}^\cdot]$  represents the mean local concentration of  $\text{Cl}^\cdot$  around the  $\text{PhCH}_2^\cdot$  radicals. We assume that each pair in the interaction is independent of the others and that at the instant  $t = 0$  the radicals are uniformly spaced between the distances  $\rho_1\sigma$  and  $\rho_2\sigma$  in a space of spherical symmetry and perform the following change of variables:

$$\tau = \frac{Dt}{\sigma^2} \qquad \rho = \frac{r}{\sigma}$$

It is now possible to calculate the variations in the mean local concentration of  $\text{Cl}^\cdot$  in the medium using the Laplace transform  $y$  of  $[\text{Cl}^\cdot]$ :

$$y = \int_0^\infty \exp(-st) [\text{Cl}^\cdot](t) dt$$

which leads to

$$sy - [\text{Cl}^\cdot]_0 = \frac{d^2y}{d\rho^2} + \frac{2}{\rho} \frac{dy}{d\rho} - \gamma y$$

As shown in Fig. 2, we find three different  $y$  functions (between 1 and  $\rho_1$ , between  $\rho_1$  and  $\rho_2$  and finally between  $\rho_2$  and infinity) by assuming the continuity of  $y$  and of its derivative with respect to  $\rho_1$  and  $\rho_2$ .

However, there exists a supplementary limiting condition related to the reaction of  $\text{Cl}^\cdot$  with  $\text{PhCH}_2^\cdot$ . This must be that the flux of  $\text{Cl}^\cdot$  towards  $\text{PhCH}_2^\cdot$  is equal to the quantity of  $\text{Cl}^\cdot$  which reacts at the distance  $\sigma$ , *i.e.*

$$\left(\frac{dy_1}{d\rho}\right)_{\rho=1} = \beta y_1(1)$$

If now, for simplicity, we assume  $\rho_2 - \rho_1 \ll 1$ , the analytical solution to these equations leads to

$$y_1 = A_1 \frac{\exp\{-(s + \gamma)^{1/2}\}}{\rho} + B_1 \frac{\exp\{(s + \gamma)^{1/2}\}}{\rho}$$

$$y_2 = \frac{1}{s + \gamma} + A_2 \frac{\exp\{-(s + \gamma)^{1/2}\}}{\rho} + B_2 \frac{\exp\{-(s + \gamma)^{1/2}\}}{\rho}$$

$$y_3 = A_3 \frac{\exp\{-(s + \gamma)^{1/2}\}}{\rho}$$

from which we obtain

$$y_{1,1} \propto \frac{1}{(s + \gamma)^{1/2} + \beta + 1} \frac{X}{Y} \frac{1}{\rho_1}$$

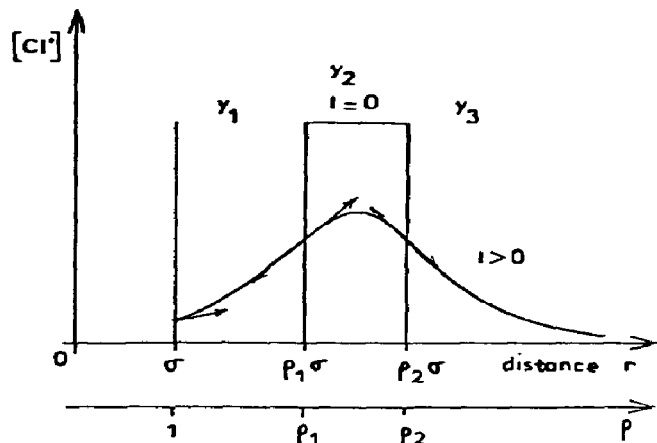


Fig. 2. Variations in the mean local concentration of  $\text{Cl}^-$  as a function of time:

$$\left(\frac{dy_1}{d\rho}\right)_1 = \beta y_1(1)$$

$$y_1(\rho_1) = y_2(\rho_1)$$

$$y_2(\rho_2) = y_3(\rho_2)$$

$$y_3(\rho) \rightarrow 0 \text{ when } \rho \rightarrow \infty$$

$$\left(\frac{dy_1}{d\rho}\right)_{\rho_1} = \left(\frac{dy_2}{d\rho}\right)_{\rho_1}$$

$$\left(\frac{dy_2}{d\rho}\right)_{\rho_2} = \left(\frac{dy_3}{d\rho}\right)_{\rho_2}$$

where  $X = \exp\{-(s + \gamma)^{1/2}\}$  and  $Y = \exp\{-(s + \gamma)^{1/2}\rho_1\}$ , and the following expression for the transform  $p$  for the yield of recombination:

$$p = \frac{1}{s} \frac{\beta}{(s + \gamma)^{1/2} + \beta + 1} \frac{X}{Y} \frac{1}{\rho_1}$$

This expression allows us to calculate  $\phi_r$  when the time tends to infinity ( $s \rightarrow 0$ ) which corresponds to the conditions of continuous excitation. We obtain

$$\phi_r = \frac{\beta}{\gamma^{1/2} + \beta + 1} \frac{\exp\{\gamma^{1/2}(1 - \rho_1)\}}{\rho_1}$$

which reverts to the expression given in ref. 5 when  $\rho_1 = 1$ .

### 2.1. Verification of the model

We use the proposal of Noyes [8] that  $\rho_1$  can be related to the viscosity of the medium by a relation of the form

$$\rho_1 = 1 + \frac{u}{\eta}$$

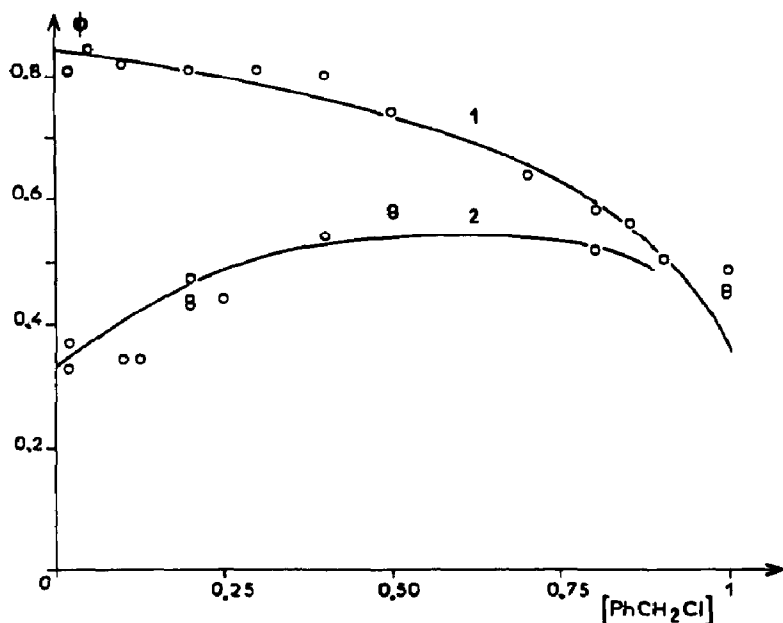


Fig. 3. Variations of  $\phi_{\text{HCl}}$  with  $[\text{PhCH}_2\text{Cl}]$  ( $\theta = 50^\circ\text{C}$ ): curve 1, decane- $\text{PhCH}_2\text{Cl}$  mixture; curve 2, decane-paraffin- $\text{PhCH}_2\text{Cl}$  mixture.

where  $u$  is a constant which is a function of the excess energy possessed by the two partners in the solvent cage and of their mass, and look for the parameters  $\beta$  and  $u$  which lead to the best agreement, in a least-squares sense, between the experimental results and the model.

It is shown in Fig. 1, and additionally in Fig. 3, that there is good agreement between the theoretical model and the measurements for

$$\beta \approx 110$$

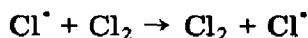
$$u \approx 0.5$$

that is  $\rho_1\sigma \approx 9 \text{ \AA}$  for  $\eta = 1 \text{ cP}$ . The value of  $\beta$  obtained then corresponds approximately to a constant  $k_c$  which is very large with respect to  $k_d$ .

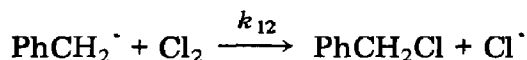
## 2.2. Influence of molecular chlorine on the initiation kinetics

As shown above the initiation kinetics depend on the efficiency of recombination in the enlarged cage between the two interacting species  $\text{Cl}^\cdot$  and  $\text{PhCH}_2^\cdot$  and also, through  $\gamma$ , on the reactivity of the medium which, in the absence of dissolved molecular chlorine, is essentially represented by processes (4) and (5).

The addition of chlorine is likely to change the yield of recombination considerably by modifying  $\gamma$  as a result of the following new processes:



the spatial displacement of  $\text{Cl}^\cdot$  which does not modify the chlorine concentration;



a process which modifies the concentration of  $\text{PhCH}_2\dot{\phantom{C}}$  and of  $\text{Cl}_2$ .

In chain radical reactions the rate constant of the second process is considered to be very large and is almost diffusion limited. The addition of  $\text{Cl}_2$  then has two opposite effects which lead to the following: a decrease in  $[\text{PhCH}_2\dot{\phantom{C}}]$  which results in an increase in the initiation yield; an increase in the local concentration of  $\text{Cl}\dot{\phantom{C}}$  which can react with another chlorine atom present in the enlarged cage leading to a decrease in the initiation yield. However, if the  $\text{PhCH}_2\dot{\phantom{C}}$  radicals are replaced by  $\text{Cl}\dot{\phantom{C}}$  radicals via process (4), the diffusion coefficients of  $\text{Cl}\dot{\phantom{C}}$  and  $\text{PhCH}_2\dot{\phantom{C}}$  are almost equal and the rate constants of the reactions  $\text{PhCH}_2\dot{\phantom{C}} + \text{Cl}\dot{\phantom{C}}$  and  $\text{Cl}\dot{\phantom{C}} + \text{Cl}\dot{\phantom{C}}$  are almost equal (which is approximately the case), the results of the recombination reaction will be unaffected, *i.e.* the yield  $\phi_r$  calculated in the absence of chlorine will remain unchanged in the presence of chlorine. Thus the quantum yield of initiation of the photochlorination of benzyl chloride can be calculated from the quantum yield of its photolysis.

### 3. Calculation of the yield of recombination of $\text{R}\dot{\phantom{C}}$ and $\text{PhCH}_2\dot{\phantom{C}}$ : a second cage reaction

In the presence of a hydrocarbon (decane in particular), the  $\text{Cl}\dot{\phantom{C}}$  radicals disappear from the medium essentially by process (5). Under these conditions the rather unreactive  $\text{PhCH}_2\dot{\phantom{C}}$  radicals and the new equally unreactive  $\text{R}\dot{\phantom{C}}$  radicals are formed in the cage. As these radicals are close to one another, they have a greater probability of recombining. Under these conditions the yield of  $\text{PhCH}_2\text{—R}$  must be very much greater than that of  $\text{R—R}$  and  $\text{PhCH}_2\text{—PhCH}_2$ . The results given in Table 1 show that this is indeed the case.

If we assume as a first approximation that the rate constant for the cross-reaction is approximately equal to twice the square root of the constants  $k_6$  and  $k_8$  (this assumption was approximately verified in earlier work [7]), *i.e.*

$$k_9 \approx 2(k_6 k_8)^{1/2}$$

it is possible to estimate the fraction of the recombination of  $\text{PhCH}_2\text{—R}$  that occurs outside the cage. The species  $\text{PhCH}_2\dot{\phantom{C}}$  and  $\text{R}\dot{\phantom{C}}$  formed outside the cage are assumed to be distributed in an approximately homogeneous fashion, and the product yields are

$$\phi_{\text{PhCH}_2\text{—CH}_2\text{Ph}} = \frac{k_6 [\text{PhCH}_2\dot{\phantom{C}}]^2}{(k_8^{1/2} [\text{R}\dot{\phantom{C}}] + k_6^{1/2} [\text{PhCH}_2\dot{\phantom{C}}])^2} \approx 0.325$$

$$\phi_{\text{R—R}} = \frac{k_8 [\text{R}\dot{\phantom{C}}]^2}{(k_8^{1/2} [\text{R}\dot{\phantom{C}}] + k_6^{1/2} [\text{PhCH}_2\dot{\phantom{C}}])^2} \approx 0.014$$



TABLE 1

Dimers produced in the photolysis of benzyl chloride in *n*-decane

| Mass | Number of chlorine atoms per molecule | Structure   | Percentage by weight |
|------|---------------------------------------|---|----------------------|
| 182  | 0                                     | C <sub>6</sub> H <sub>5</sub> -CH <sub>2</sub> -CH <sub>2</sub> -C <sub>6</sub> H <sub>5</sub>                | 15                   |
| 232  | 0                                     | C <sub>6</sub> H <sub>5</sub> -CH <sub>2</sub> -(CH <sub>2</sub> ) <sub>9</sub> -CH <sub>3</sub> <sup>a</sup> | 38.5                 |
| 266  | 1                                     | C <sub>6</sub> H <sub>5</sub> -CHCl-(CH <sub>2</sub> ) <sub>9</sub> -CH <sub>3</sub>                          | 3.3                  |
| 282  | 0                                     | CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>9</sub> -(CH <sub>2</sub> ) <sub>9</sub> -CH <sub>3</sub>            | ≈0                   |

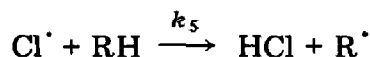
[PhCH<sub>2</sub>Cl] = 0.078 mol l<sup>-1</sup>; λ = 254 nm; θ = 40 °C.<sup>a</sup>The chromatographic analysis allows us to detect five isomers arising from the addition of the benzyl radical to the decyl radical.

Therefore

$$\begin{aligned} \phi_{\text{PhCH}_2\text{-R}}(\text{outside the cage}) &= \frac{k_9[\text{R}^\cdot][\text{PhCH}_2^\cdot]}{(k_8^{1/2}[\text{R}^\cdot] + k_6^{1/2}[\text{PhCH}_2^\cdot])^2} \\ &= 2(\phi_{\text{PhCH}_2\text{-CH}_2\text{Ph}}\phi_{\text{RR}})^{1/2} \\ &= 0.13 \end{aligned}$$

which is much less than the value of 0.66 obtained experimentally.

Since the theory presented above for a secondary cage effect is reasonable, we have developed an extension of the cage diffusional model presented in this paper. In order to do this we looked for variations in the local concentration of R<sup>·</sup> formed by the process



Then the mean local concentration of R<sup>·</sup> must obey the following diffusion equations:

$$\frac{\partial[\text{R}^\cdot]}{\partial t} = D \nabla^2[\text{R}^\cdot] + k_5[\text{RH}][\text{Cl}^\cdot]$$

$$\left(\frac{\partial[\text{R}^\cdot]}{\partial \rho}\right)_\sigma = \beta'[\text{R}^\cdot]_\sigma$$

where β' = k<sub>9</sub>/k<sub>d</sub>. The solution of this system on passing into Laplace space leads to a reaction yield in the cage which is given by

$$\phi = \frac{\beta'}{\beta' + 1} \frac{1}{\rho_1} \left[ 1 - \exp\{\gamma^{1/2}(1 - \rho_1)\} \frac{\beta + 1}{\gamma^{1/2} + \beta + 1} \right]$$

Thus for the values of  $\beta$  and  $\rho_1$  defined above

$$\phi \approx 0.41 \frac{\beta'}{\beta' + 1}$$

Now experimentally the yield obtained is of the order of

$$\phi_{\text{HCl}} \{ \phi_{\text{PhCH}_2\text{-R}} - \phi_{\text{PhCH}_2\text{R}}(\text{outside the cage}) \}$$

*i.e.* 0.42. When all the assumptions made are taken into account this calculation shows that the constant of recombination between  $\text{PhCH}_2\dot{\text{C}}$  and  $\text{R}\dot{\text{C}}$  must be greater than the diffusion constant  $4\pi N\sigma D$ , *i.e.*  $k_9 > k_d$ . In any case there is a reasonably good agreement between the experimental results and the simplified model presented here which demonstrates a second cage effect due to the reaction of  $\text{Cl}\dot{\text{C}}$  with RH.

## References

- 1 J. C. André, A. Tournier, X. Deglise and M. Niclaude, *J. Photochem.*, 18 (1981) 57.
- 2 A. Tournier, *Thèse de Doctorat d'Etat*, Nancy, 1982.
- 3 J. Hyomaki and J. Koskikallio, *Acta Chem. Scand., Ser. A*, 31 (1977) 321.
- 4 T. Ichimura and Y. Mori, *J. Chem. Phys.*, 57 (4) (1972) 1677.
- 5 J. C. André, M. Bouchy and M. Niclaude, *React. Kinet. Catal. Lett.*, 11 (1979) 289.
- 6 W. A. Pryor, *Free Radicals*, McGraw-Hill, New York, 1966, pp. 181 - 188.
- 7 J. C. André, *Thèse de Doctorat d'Etat*, Nancy, 1971.  
J. C. André, F. Baronnet, M. Niclaude and J. Lemaire, *J. Chim. Phys.*, 68 (1971) 1177 - 1182.
- 8 R. M. Noyes, *Prog. React. Kinet.*, 1 (1961) 129.