

KINETICS OF THE PHOTOCHEMICAL FLUORINATION OF CARBONYL FLUORIDE*

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(Received November 9, 1973)

Summary

The kinetics of the photochemical gas phase fluorination of CF_2O has been studied between 15° and 80°C in cells of quartz and of aluminium. The only products formed are CF_3OF and the peroxide $(\text{CF}_3\text{O})_2$.

The reaction rate is proportional to the first power of the light intensity. The quantum efficiency of the CF_2O consumption, $\Phi_{\text{CF}_2\text{O}}$, increases with increasing CF_2O pressure up to a maximum value of $2 \text{ mol}/h\nu$ and is independent of the total pressure and the fluorine pressure:

$$\Phi_{\text{CF}_2\text{O}} = \frac{2 |\text{CF}_2\text{O}|}{k + |\text{CF}_2\text{O}|} \quad (\text{I})$$

The ratio $(\text{CF}_3\text{O})_2/\text{CF}_3\text{OF}$, R , increases proportionally to $P_{\text{CF}_2\text{O}}$ and is independent of $P_{\text{tot.}}$ and P_{F_2} .

$$R = k' |\text{CF}_2\text{O}| \quad (\text{II})$$

The F_2 consumption is independent of P_{F_2} but increases at low pressures rather rapidly with $P_{\text{CF}_2\text{O}}$, passing through a maximum and then decreasing slowly. Φ_{F_2} can reach values somewhat higher than $1 \text{ mol}/h\nu$.

$$\Phi_{\text{F}_2} = \Phi_{\text{CF}_2\text{O}} \frac{1 + k' |\text{CF}_2\text{O}|}{1 + 2 k' |\text{CF}_2\text{O}|} \quad (\text{III})$$

A certain wall effect can be observed. Changing from the quartz to the aluminium cell $\Phi_{\text{CF}_2\text{O}}$ is slightly reduced, whereas the R values increase in a more pronounced way.

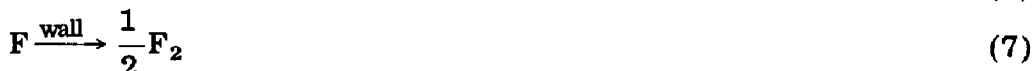
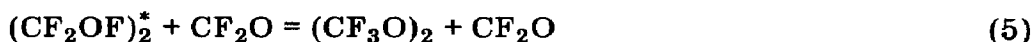
O_2 has an inhibiting effect which increases with increasing P_{O_2} and decreases with increase of temperature.

$$\Phi_{\text{CF}_2\text{O}} = \frac{4 |\text{CF}_2\text{O}|}{[(|\text{CF}_2\text{O}| + k)^2 + 8 I_{\text{abs}} \cdot k'' |\text{O}_2|]^{1/2} + |\text{CF}_2\text{O}| + k} \quad (\text{IV})$$

There are no chains, but the reaction is a very complex one.

* Taken from the Doctoral Thesis of M.I.L. (1972).

The experimental results can be explained with the following reaction scheme:



Applying the stationary-state treatment this mechanism leads to eqns.

(I) - (IV), resulting in $k = k_7/k_2$; $k' = k_5/2k_4$ and $k'' = k_9k_8/k_2^2k'_8$.

From the temperature coefficients of k , k' and k'' and assuming that $E_7 = 0$; $E_8 = 0$ and $E_9 \cong 3$ kcal, the following activation energies are obtained: $E_2 = 6.2$ kcal, $E_5 - E_4 = 5$ kcal and $E_8 = 11 \pm 3$ kcal.

Introduction

The fluorination of CF_2O has been treated before in several papers. The catalytic reaction was thoroughly investigated by Cady [1] and coworkers, whereas the light reaction, mainly for preparative purposes, was studied by Aymonino [2]. Working with the complete radiation of a high pressure mercury lamp, Aymonino found that the reaction products were essentially CF_3OF and $(\text{CF}_3\text{O})_2$. His data, however, were not sufficient to elaborate a reaction scheme.

In the following a kinetic study of the photochemical gas phase fluorination of CF_2O is presented with the purpose of establishing the mechanism of this reaction and of determining the Arrhenius parameters of its partial reactions.

Experimental

Preliminary experiments confirmed that the reaction occurred with a decrease of pressure. Separations of the products made at low temperature together with i.r. spectra of each of the fractions showed that the only products formed were CF_3OF and $(\text{CF}_3\text{O})_2$. The course of the reaction was

therefore followed by a manometric static method at constant volume and temperature by measuring the decrease of the total pressure at certain time intervals.

The apparatus [3] consisted mainly of a cylindrical quartz cell, 10 cm long with an inside diameter of 4.6 cm, having flat, optical polished front windows. The quartz cell was in some experiments replaced by another one of suitable pre-fluorinated aluminium of similar size to the first but having fluorite windows. By means of a quartz capillary and a quartz "T" it was connected on one side to a Bodenstein quartz spiral manometer used as a zero instrument and on the other side through a metal valve to the set of storing traps and balloons and to the vacuum system.

The cells were mounted in a specially constructed metal box 20 cm long, 15 cm wide and 15 cm deep which permitted the light beam to enter the system without crossing the circulating water. Constant temperature (± 0.2 °C) during the experiments, which were performed between 15 ° and 80 °C, was obtained by using a Haake thermostat.

A 200 W Osram HBO mercury lamp was used as light source. A centred optical system and a combination of a UG2 and a WG3 Schott & Gen. Mainz, 2 mm thick glass filters permitted a parallel, homogeneous and practically monochromatic (365 nm) light beam of about 4 cm diameter to be obtained.

The intensity of the incident light, of the order of $10^{19} h\nu/\text{min}$, was periodically determined by actinometry in the same reactor cell measuring the photochemical decomposition of oxygen difluoride [4].

The light absorbed by fluorine was calculated from its extinction coefficient ($\epsilon = 6.61 \times 10^{-5} \text{ Torr}^{-1}$ for $T = 30$ °C) and its pressure.

In order to determine the influence of the light intensity on the reaction rate some experiments were performed inserting a calibrated metal screen in the light path.

Preparation of gases

CF₂O of sufficient purity was not available. It therefore was prepared in the laboratory by photolyzing F₂ with light of 365 nm in the presence of oxalyl fluoride. By careful control of the photolysis time it was possible to produce CF₂O accompanied by only small amounts of CF₃OF and (CF₃O)₂. Pure CF₂O (more than 95%) was obtained by repeated low temperature bulb-to-bulb vacuum distillation. I.r. spectra showed the remainder to consist of CF₃OF.

Oxalyl fluoride was prepared by refluxing oxalyl chloride with sodium fluoride in acetonitrile, using essentially the method of Tullock and Coffman [5].

Fluorine from a cylinder (Matheson Co.) was passed through a trap cooled with liquid oxygen and stored in liquid nitrogen.

Carbon dioxide was obtained by repeatedly sublimating dry ice from trap to trap under vacuum and finally storing it in a 2 l balloon.

Oxygen and nitrogen were obtained from commercial cylinders and purified by conventional methods.

Oxygen difluoride from a cylinder (Matheson Co.) was passed through a trap cooled with liquid oxygen and stored in a 2 l balloon kept in darkness.

Procedure

The thermostat temperature was adjusted and the lamp was switched on. Then, the reactants were introduced into the reaction cell and illuminated at known time intervals. The pressure readings were always taken when the system remained in darkness.

In most of the experiments the reaction was followed until the reactant which was in defect was consumed more than 50%. Since CF_3OF and $(\text{CF}_3\text{O})_2$ were the only products formed according to the stoichiometry, it was possible to establish the following relations:

$$[\text{CF}_2\text{O}]_{\text{consd}} = [\text{CF}_3\text{OF}]_{\text{formd}} + 2 [(\text{CF}_3\text{O})_2]_{\text{formd}} = \Sigma \Delta p$$

$$[(\text{CF}_3\text{O})_2]_{\text{formd}} = \Sigma \Delta p - [\text{F}_2]_{\text{consd}}$$

$$[\text{CF}_3\text{OF}]_{\text{formd}} = 2[\text{F}_2]_{\text{consd}} - \Sigma \Delta p$$

$$\frac{\Delta p}{\Delta t} = - \frac{d[\text{CF}_2\text{O}]}{dt}$$

in which $[\text{CF}_2\text{O}]_{\text{consd}}$, $[\text{F}_2]_{\text{consd}}$, $[(\text{CF}_3\text{O})_2]_{\text{formd}}$, $[\text{CF}_3\text{OF}]_{\text{formd}}$ are the amounts of the indicated gases consumed or respectively formed, in Torr. Δt is the time interval in min, Δp the corresponding pressure decrease and $\Sigma \Delta p$ the decrease of the total pressure at the end of the experiment.

At the end of each run the reaction mixture was pumped through a U tube held at -185°C . In this way the excess of F_2 was eliminated and measured. By means of low temperature distillation of the condensed fraction the amount of the peroxide and the sum of CF_3OF and the excess of CF_2O were determined.

With these data and the preceding relations it was possible to calculate the amounts of $(\text{CF}_3\text{O})_2$ and CF_3OF formed and consequently also the ratio $R = (\text{CF}_3\text{O})_2/\text{CF}_3\text{OF}$. In some experiments, by a careful low temperature distillation, a separation of the CF_3OF and the excess of CF_2O was carried out. Results were coincident with the calculated data.

In order to obtain information about the F_2 consumption during the course of the reaction, in several experiments the photolysis was interrupted when the pressure decrease was about 10 Torr. Fluorine was then pumped off and measured. Afterwards the original fluorine pressure was restored and the photolysis continued up to a new 10 Torr Δp and so on.

Results

In order to determine the influence of the different parameters on the reaction rate and to establish the corresponding rate equation, a number of

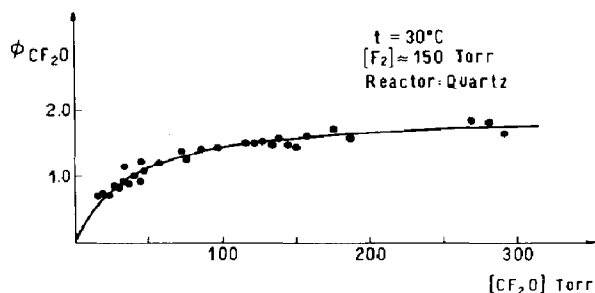


Fig. 1. $\Phi_{\text{CF}_2\text{O}}$ vs. $|\text{CF}_2\text{O}|_{\text{Torr}}$ at 30 °C.

experiments were realized at 15 °, 30 °, 60 ° and 80 °C in systems free of oxygen and in systems containing known amounts of this gas.

Oxygen free systems

The results obtained in experiments in which the light intensity was varied showed that the reaction rate was proportional to the first power of the absorbed light. The quantum efficiency of CF_2O consumption, $\Phi_{\text{CF}_2\text{O}} = -(1/I_{\text{abs.}})(d|\text{CF}_2\text{O}|/dt)$, is consequently independent of the light intensity.

In order to determine the influence of CF_2O its pressure was varied between 10 and 500 Torr. Two effects were observed, one on $\Phi_{\text{CF}_2\text{O}}$ and the other one on the R ratio. $\Phi_{\text{CF}_2\text{O}}$ increases at low pressure linearly with CF_2O approaching a limit at higher pressures. At every temperature, this dependence can be represented by means of the equation:

$$\Phi_{\text{CF}_2\text{O}} = \frac{2|\text{CF}_2\text{O}|}{k + |\text{CF}_2\text{O}|} \quad (\text{I})$$

in which k is a temperature dependent constant. In Table 1 the best k values at each temperature, calculated by least-squares, are given.

TABLE 1

T (°C)	15	30	50	80
k_{Torr}	49	38	18	7

Figure 1 shows $\Phi_{\text{CF}_2\text{O}}$ at 30 °C as a function of CF_2O pressure. The points are experimental values whereas the curve was calculated with eqn. (I).

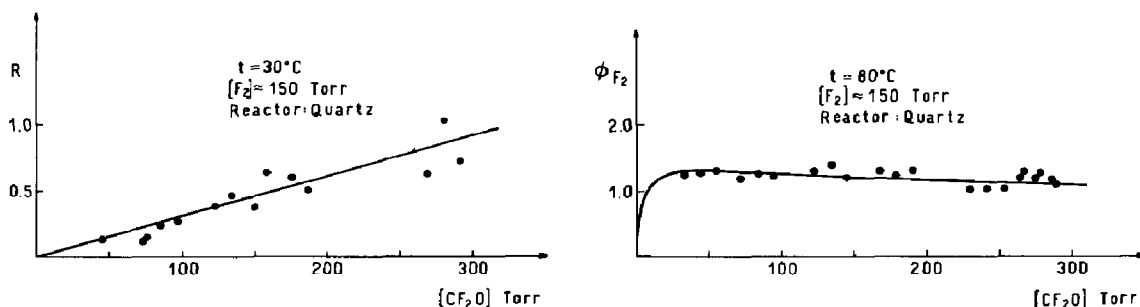
The ratio R increases at each temperature linearly with the CF_2O pressure:

$$R = \frac{|(\text{CF}_3\text{O})_2|}{|\text{CF}_3\text{OF}|} = k'|\text{CF}_2\text{O}| \quad (\text{II})$$

In Table 2 the best k' values at each temperature, calculated by least-squares, are given.

TABLE 2

$T(^{\circ}\text{C})$	15	30	50	80
$k' \times 10^3 (\text{Torr}^{-1})$	2.0	3.1	4.5	10.8

Fig. 2. R vs. $|\text{CF}_2\text{O}|_{\text{Torr}}$ at 30°C .Fig. 3. Φ_{F_2} vs. $|\text{CF}_2\text{O}|_{\text{Torr}}$ at 80°C .

In Fig. 2 some of the R values obtained at 30°C are represented as a function of the corresponding CF_2O pressures. The "theoretical" curve was drawn with eqn. (II) and $k' = 3.1 \times 10^{-3} \text{Torr}^{-1}$.

Experiments in which the fluorine pressure was varied between 50 and 570 Torr, showed that the fluorine concentration had no effect on $\Phi_{\text{CF}_2\text{O}}$ and R .

The experiments in which the amount of the reacted F_2 was determined for each Δp , allowed the quantum efficiency of the fluorine consumption, Φ_{F_2} to be calculated. It was found that Φ_{F_2} did not depend on fluorine pressure, that it increased rather rapidly at low CF_2O pressure, passing later on through a maximum and then decreasing slowly. It is important to note that Φ_{F_2} can have values greater than 1, which indicates that some non-photolyzed fluorine must be consumed.

From the stoichiometry and the R ratio the following equation is deduced:

$$\Phi_{\text{F}_2} = \Phi_{\text{CF}_2\text{O}} \cdot \frac{1 + k'|\text{CF}_2\text{O}|}{1 + 2k'|\text{CF}_2\text{O}|} \quad (\text{III})$$

Figure 3 represents some of the results obtained at 80°C . At this temperature the CF_2O pressure has a rather pronounced effect on Φ_{F_2} . The circles are experimental values, whereas the "theoretical" curve is drawn with eqn. (III) and $k' = 10.8 \times 10^{-3} \text{Torr}^{-1}$.

The influence of the reaction products and of the total pressure on the course of the reaction was studied by adding products up to 150 Torr and CO_2 or N_2 up to 600 Torr to the reaction mixture. No effect on $\Phi_{\text{CF}_2\text{O}}$ and R could be observed.

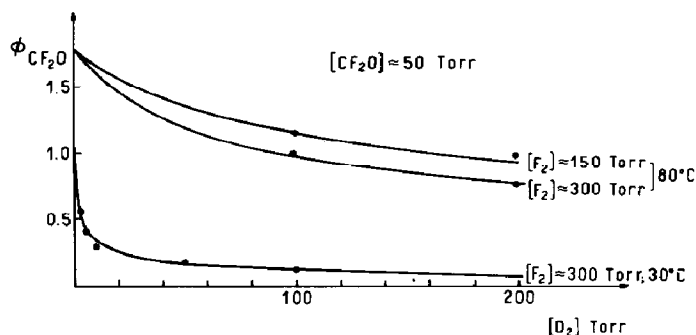


Fig. 4. $\Phi_{\text{CF}_2\text{O}}$ vs. $|\text{O}_2|_{\text{Torr}}$.

By changing the quartz cell with the aluminium reactor it could be shown that there existed some wall effects. $\Phi_{\text{CF}_2\text{O}}$ was slightly reduced and the R values showed a marked reduction. The linear dependence of R on the CF_2O pressure was maintained but with $k'_{30^\circ\text{C}} = 0.8 \times 10^{-3} \text{ Torr}^{-1}$.

Systems containing oxygen

A series of experiments were carried out in the presence of oxygen, in amounts ranging from 2 to 200 Torr. According to the results obtained, oxygen has an inhibiting effect on $\Phi_{\text{CF}_2\text{O}}$ which increases with increasing pressure of O_2 and decreases with the increase of temperature and CF_2O pressure. On the other hand, at constant temperature the inhibiting effect of O_2 increases with the amount of light absorption.

Although the nature of the reaction products is not affected by O_2 , the R ratio decreases. Figure 4 demonstrates the O_2 effect at 30°C and 80°C on $\Phi_{\text{CF}_2\text{O}}$. The curves were calculated with eqn. (IV). The cricles are experimental points.

Discussion

Under our experimental conditions no dark reaction could be observed. The measurements correspond therefore exclusively to the photochemical reaction.

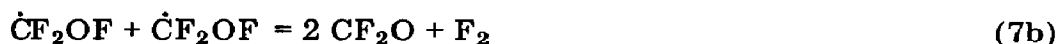
The primary process consists without any doubt of the dissociation of the F_2 molecules, which has to be followed by the reactions of the F atoms with CF_2O molecules. There are two possibilities and either $\text{CF}_3\text{O}'$ or $\dot{\text{C}}\text{F}_2\text{OF}$ radicals may be produced. As it is a well known fact that $\text{CF}_3\text{O}'$ radicals recombine readily forming $(\text{CF}_3\text{O})_2$ and only small quantities of this compound are produced, it can be concluded that it is the $\dot{\text{C}}\text{F}_2\text{OF}$ radical which is formed in this reaction.



The upper limit of $2 \text{ mol}/h\nu$ for $\Phi_{\text{CF}_2\text{O}}$ shows that there are no chains.

$\Phi_{\text{CF}_2\text{O}}$ values smaller than 2 mol/h ν indicate that either a part of the F atoms is consumed in reactions other than reaction (2) or that the $\dot{\text{C}}\text{F}_2\text{O}\dot{\text{F}}$ radicals or some other intermediaries may react reforming the reactants.

The reactions to consider are:



However, only reaction (7) is consistent with the independence of $\Phi_{\text{CF}_2\text{O}}$ from light intensity.

Diffusion is too slow a process in order to explain the rate of F atoms consumption. It furthermore should be accompanied by a dependency of $\Phi_{\text{CF}_2\text{O}}$ on the total pressure, which was not found. Considering that the reaction is exothermic ($\text{F} + 1/2 \text{F}_2 + \text{CF}_2\text{O} = \text{CF}_3\text{O}\dot{\text{F}}$; $\Delta H = -47.6$ kcal) it can be assumed that in the transference of the F atoms from the bulk to the wall convection plays an important role.

As $\Phi_{\text{CF}_2\text{O}}$ is independent of R , the rate constants of the partial reactions by which the products are formed will not appear in the total rate equation.

Assuming that the F atoms are produced in step (1) and consumed in steps (2) and (7), by means of Bodenstein's steady-state treatment it can be deduced that:

$$\Phi_{\text{CF}_2\text{O}} = \frac{2|\text{CF}_2\text{O}|}{k_7/k_2 + |\text{CF}_2\text{O}|} \quad (\text{V})$$

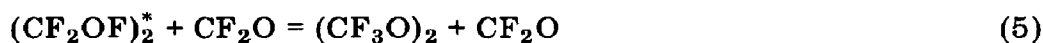
This expression is identical with the experimentally found eqn. (I) by taking $k_7/k_2 = k$. k_7 represents the constant of a complex process involving the way by which the F atoms reach the wall and wall efficiency in the recombination process.

From an Arrhenius plot of the rate constant k it follows that $E_2 - E_7 = 6.2$ kcal. E_7 is not known but it can be assumed to be very small or even negative. Taking $E_7 = 0$, the value 6.2 kcal corresponds to the activation energy of reaction (2), $E_2 = 6.2$ kcal.

The nature of the intermediates could not be experimentally established and consequently the partial reactions of the mechanism are given on a somewhat speculative basis.

The mechanism must be able to explain the influence of the CF_2O pressure, the temperature and the wall effects on the R ratio together with the independence of this ratio from fluorine and the total pressure. For these reasons it must be certainly a complex one. Furthermore, it has to be considered that the upper limit of $\Phi_{\text{CF}_2\text{O}}$ is 2 mol/h ν . This means that two CF_2O molecules are consumed for each quantum of light absorbed by F_2 , independently of the values that might reach R . This indicates that in the formation of 1 mol of $\text{CF}_3\text{O}\dot{\text{F}}$, $1/2$ mol (photolyzed) and $1/2$ mol (non-photolyzed) fluorine must be consumed. Accordingly, Φ_{F_2} can reach values somewhat higher than 1 mol/h ν .

The simplest mechanism consistent with all the observed experimental facts is the one composed of reactions (1) and (2) followed by:



By a steady state treatment it can be deduced that $R = k_5/2k_4|\text{CF}_2\text{O}|$ which is identical with the experimentally found eqn. (II) taking $k' = k_5/2k_4$. From an Arrhenius plot of k' , $E' = E_5 - E_4 = 5$ kcal is obtained.

Step (3) is a bimolecular association reaction between two radicals, producing an activated molecule $(\text{CF}_2\text{OF})_2^*$. Since the total pressure has no influence on the reaction rate, it is assumed that this molecule is rather indifferent with respect to collisions. It can undergo either an internal conversion to another excited state, step (4), or may react with CF_2O , step (5).

For the same reason, the $(\text{CF}_2\text{OF})_2'$ molecule must also be stable with respect to collisions and finally react with F_2 , step (6), forming CF_3OF .

Reaction (5) should be a real chemical reaction which involves the production of $(\text{CF}_3\text{O})_2$ and the reforming of CF_2O .

The observed decrease of R in the aluminium reactor shows that there is a specific wall effect. This can be taken into account by including in the mechanism reaction (4'): $(\text{CF}_2\text{OF})_2^* \xrightarrow{\text{wall}} \text{CF}_3\text{OF} + \text{CF}_2\text{O}$ with a small effect in the case of the quartz reactor and a more pronounced one in the case of the aluminium reactor. The relatively small difference between the $\Phi_{\text{CF}_2\text{O}}$ values in the two reactors can be explained assuming that the fluorinated aluminium surface has approximately the same efficiency for the recombination of F atoms as quartz.

The inhibiting effect of oxygen can be interpreted with the formation of FO_2 radicals [6] and a following reaction with F atoms:



Assuming that reaction (9) does not affect the equilibrium (8) the following equation can be deduced:

$$\Phi_{\text{CF}_2\text{O}} = \frac{4|\text{CF}_2\text{O}|}{[(|\text{CF}_2\text{O}| + k_7/k_2)^2 + 8 I_{\text{abs.}} \cdot k_9 k_8 / k_2^2 k_8' |\text{O}_2|]^{1/2} + |\text{CF}_2\text{O}| + k_7/k_2} \quad (\text{VI})$$

which is identical with the experimentally found eqn. (IV) by taking $k_7/k_2 = k$ and $k_9 k_8 / k_2^2 k_8' = k''$.

With $|\text{O}_2| = 0$, eqn. (VI) is transformed into eqn. (I) which holds as shown before for the oxygen free system.

From the experiments made at 30 ° and 80 °C the following k'' values were obtained:

T (°C)	30	80
k''_{\min}	35,000	400

With these values and eqn. (VI) the curves in Fig. 4 were drawn.

From the temperature coefficient of k'' , an apparent heat of activation $E'' = 2E_2 - E_9 - E_8 + E'_8 = 19$ kcal is obtained. E_8 is not known but most probably it is near to zero, $E_8 \cong 0$; E_9 must be small, probably between 2 and 5 kcal. Assuming $E_9 \cong 3$ kcal, $E'_8 = 11 \pm 3$ kcal. This value is in good agreement with those found in the study of other reactions [7, 8].

Finally, the observed decrease of R with increasing O_2 pressure suggests that the presence of O_2 favours the conversion of $(CF_2OF)_2^*$ into $(CF_2OF)_2'$.

References

- 1 G. H. Cady, An. Asoc. Quim. Argent., 59 (1971) 125.
- 2 P. J. Aymonino, Proc. Chem. Soc., (1964) 341.
- 3 K. L. Müller and H. J. Schumacher, Z. Phys. Chem., B35 (1937) 285.
- 4 R. Gatti, E. Staricco, J. E. Sicre and H. J. Schumacher, Z. Phys. Chem., NF35 (1962) 343.
- 5 G. W. Tullock and D. D. Coffman, J. Org. Chem., 25 (1960) 2016.
- 6 A. H. Jubert, J. E. Sicre and H. J. Schumacher, Z. Phys. Chem., NF67 (1969) 138.
- 7 E. J. Vasini and H. J. Schumacher, Photochem. Photobiol., 7 (1968) 755.