

KINETIC ASPECTS OF DYE-SENSITIZED PHOTO-OXYGENATION*

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Summary

A kinetic investigation is reported of the dye-sensitized photo-oxygenation of 2-methyl-2-butene and 2,3-dimethyl-2-butene, a reaction which involves singlet oxygen as intermediate species. The reaction was carried out in a gas-liquid photoreactor. Two types of régimes in which the reaction takes place exist, according to experimental conditions. At high olefin and photosensitizer concentrations, the reaction takes place in a dynamic régime and the empirical rate equation $R = kP_{O_2}$, adequately represents the phenomenon, inasmuch as the reaction rate depends only on the oxygen partial pressure in the inlet gas. This and other data reported and discussed fit the suggestion that the oxygen interphase mass transfer is the rate determining step in the specified range of experimental conditions. At low photosensitizer and olefin concentrations, the chemical régime is present. It was found that in the olefin concentration range examined, the value of β , the reactivity index of an acceptor towards singlet oxygen, was a function of concentration.

Introduction

The dye-sensitized photo-oxygenation of olefins and dienoid compounds has been the subject of much recent interest [1], mainly because it involves the intermediacy of the excited species singlet oxygen, $O_2(^1\Delta_g)$. From a chemical standpoint singlet oxygen can be visualized as a reactive dienophile which can undergo the Diels-Alder reaction with suitable dienes and the "ene" reaction with suitable olefins. This species plays a role in the photodynamic effect in living organisms [2, 3] as well as in some aspects of air pollution [4]. It can also be the product of the heterolytic decomposition of peroxides [5], as well as of u.v. photolysis of ozone [6]. Further details can be found in the work of Wayne [7].

The mechanisms of the dye-sensitized photo-oxygenation in the liquid phase have been studied by several groups [8 - 10]. With Rose Bengal,

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methylene blue and many other sensitizers the reaction starts by exciting the ground state sensitizer to the first triplet excited state (3S_1), which in turn transfers the excitation energy to the ground state molecular oxygen to produce singlet molecular oxygen, $O_2(^1\Delta_g)$:



The reactive species either decays, regenerating ground state oxygen (reaction 1) or reacts with acceptor A to give the product AO_2 (reaction 2), according to the scheme:



The instantaneous quantum yield, Φ_{AO_2} , for product formation is given by the expression:

$$\Phi_{AO_2} = \Phi_{^1O_2} \frac{k_2 [A]}{k_1 + k_2 [A]}$$

or

$$\Phi_{AO_2} = \Phi_{^1O_2} \frac{[A]}{\beta + [A]}$$

where $\Phi_{^1O_2}$ is the instantaneous quantum yield of singlet oxygen formation and β is k_1/k_2 .

Essentially the β values are an index or reactivity of particular organic acceptors towards singlet oxygen. They have been determined mostly by competitive simultaneous reactions between two acceptors and singlet oxygen, and ratios β_{A_1}/β_{A_2} can be easily deduced from the respective yields [8, 10].

An alternative procedure to obtain β is to write the preceding equation in the form [10]:

$$\frac{1}{\Phi_{AO_2}} = \frac{1}{\Phi_{^1O_2}} \left(1 + \frac{\beta}{[A]} \right)$$

This relationship is valid only if $[A]$ does not change appreciably during the course of reaction, *i.e.* for negligible conversions. By plotting $1/\Phi_{AO_2}$ against $1/[A]$ one should obtain a straight line. The ratio of slope to intercept gives β . In practice, instead of Φ_{AO_2} , the amount of product formed per unit time of irradiation $[AO_2]$ will be used since it is proportional to Φ_{AO_2} , if the light flux is constant within a series of reactions.

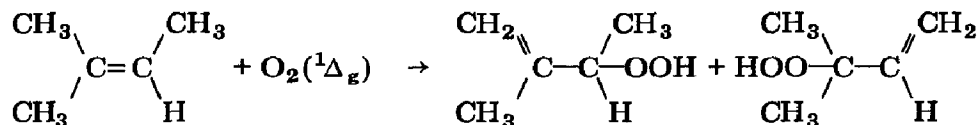
However, the β values so obtained by various authors differ greatly, both in relative values and in order of magnitude [8 - 14]. In effect the β values reported in the literature have been obtained by the two previously mentioned methods and also using different types of equipment. If one is going to use the first (competitive) method to obtain a correct β value of an

acceptor relative to a standard β value, it is most important to carry out the reaction in the chemical régime (*i.e.* determined by chemical parameters) for both acceptors. If one uses the second (absolute) method, it is also indispensable to carry out the reaction in the chemical régime for the acceptor in question. This point has to be kept in mind because the reaction in question is a gas-liquid reaction involving interphase mass transfer which could be the rate controlling step of the overall reaction. In such a situation even the type of equipment can determine the type of régime, chemical or dynamic. Some of the sophisticated experimental settings employed as chemical reactors [15 - 19], such as the cell of a spectrophotometer, use for the reaction only the small quantity of oxygen present in the solvent by Henry's law (*e.g.* $10^{-3} M$ in alcohol) and thus for very low olefin concentrations ($10^{-4} M$) we are sure to be in a chemical régime. Other reactors do not guarantee it. In any case, scarce attention has been devoted to how the type of régime could influence the kinetic analysis.

In this paper we report about a kinetic investigation of an olefin dye-sensitized photo-oxygenation carried out at room temperature and using a photoreactor which could resemble a potential industrial photochemical reactor [20, 21]. We have paid particular attention to the mass transfer problems.

Experimental

The reaction investigated was only a convenient example of the "ene" reaction [8, 11], known to occur without side reactions, according to the scheme:



2-Methyl-2-butene (Schuchardt, purity $\geq 95\%$) was used as acceptor, ethyl alcohol being the solvent. 2,3-Dimethyl-2-butene (Fluka, purity $\geq 98\%$) was also tested for comparison. All the runs were carried out at room temperature in an annular photoreactor, basically similar to the reactors described earlier [20, 22, 23]. The light source, a tungsten filament halogen 500 W or 200 W lamp, was inside the water-cooled jacket which was in turn kept immersed in the reactor. Gaseous oxygen was bubbled through the solution containing the olefin, the solvent and the photosensitizer (Carlo Erba methylene blue), after being dispersed by a porous septum. An acetone-dry ice mixture kept at -50°C was used to prevent the loss of the olefin which tended to be stripped by the gas flux.

The reaction was followed by analyzing the unconverted olefin. Facilities were arranged for withdrawing liquid samples from the reaction solution for gas chromatographic analysis. A Carlo Erba Fractovap C gas chromatograph with a thermal conductor and a 2,5-*m*-dinonylphthalate on Chromosorb G column (10% by weight) kept at 90°C was used.

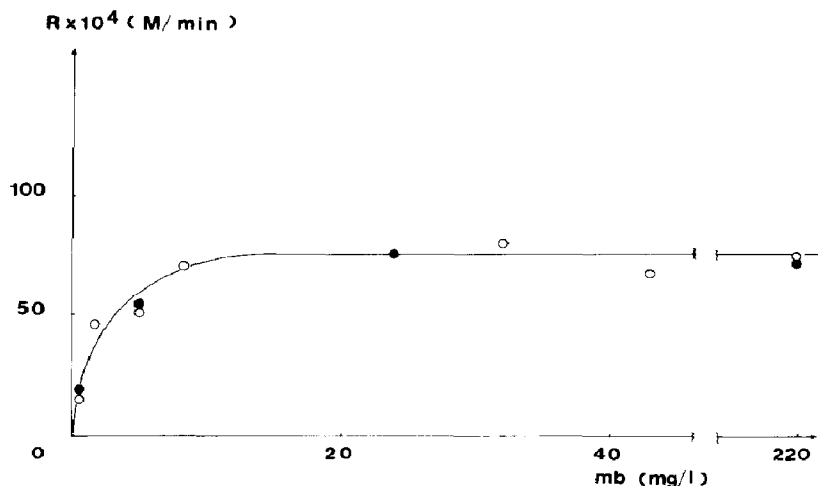


Fig. 1. Initial rate *vs.* methylene blue concentration. T = room temperature; ethyl alcohol, 260 ml; 2-methyl-2-butene, 0.366 M; gas (pure oxygen) flux, 150 cm³/min. Lamps: ○, 500 W; ●, 200 W.

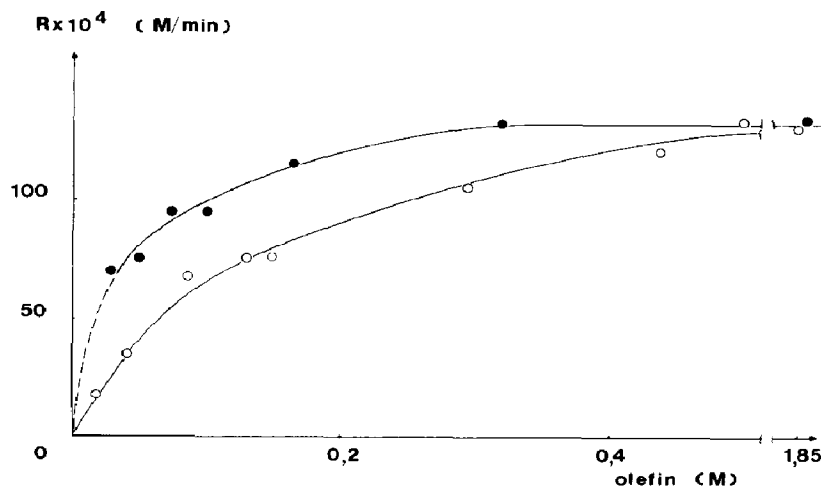


Fig. 2. Initial rate *vs.* olefin concentration. ○, 2-methyl-2-butene; ●, 2,3-dimethyl-2-butene. T = room temperature; ethyl alcohol, 260 ml; methylene blue, 260 mg/l; gas (pure oxygen) flux, 150 cm³/min.

Results

The results of the kinetic investigation of the 2-methyl-2-butene dye-sensitized photo-oxygenation are shown in Figs. 1 to 7.

In Fig. 1 we report the initial reaction rate *vs.* photosensitizer concentration, using the same light source, but with two different intensities. We can see that for concentrations higher than about 12 mg/l no reaction rate variation occurs, while the variation occurs only for concentrations smaller than 10 mg/l. The light intensity has no influence whatsoever.

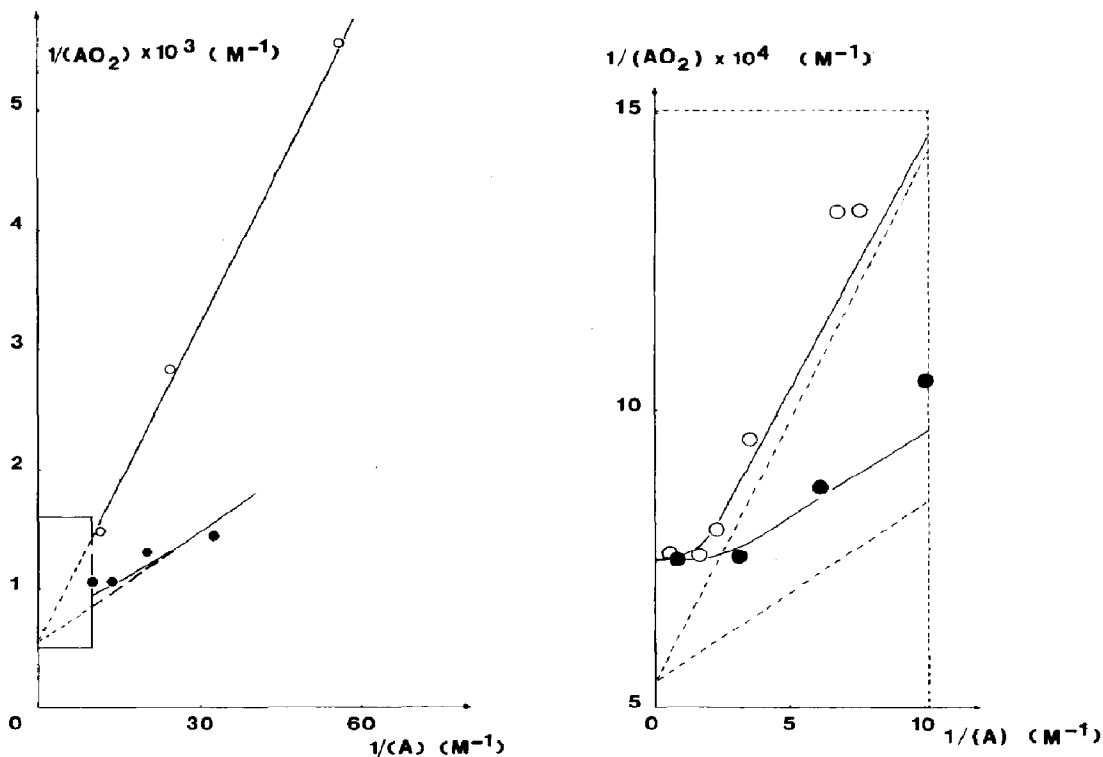


Fig. 3. $1/[AO_2]$ vs. $1/[A]$. \circ , 2-methyl-2-butene; \bullet , 2,3-dimethyl-2-butene. Data from Fig. 2.

Figure 2 shows how the reaction rate is dependent on the olefin concentration. For concentrations higher than about 0.40 M the reaction rate does not vary appreciably, while for lower concentrations it becomes concentration dependent. In Fig. 2 the initial reaction rate of 2,3-dimethyl-2-butene vs. olefin concentration is also reported. According to the values found in the literature this olefin was expected to be 20 to 50 times more reactive towards singlet oxygen than 2-methyl-2-butene used in all the other runs [8, 11, 13]. For concentrations higher than 0.40 M no significant differences between the reaction rates for the two olefins were observed; at smaller concentrations greater differences are present.

Figures 3(a) and 3(b) show the $1/[AO_2]$ vs. $1/[A]$ curves derived from experimental data shown in Fig. 2. We can see that for low concentrations this Fig. produces straight lines, analogously to other data found in the literature, but for higher concentrations (lower value of $1/[A]$) the curves diverge sensitively from the straight lines. The value of β (ratio of slope to intercept) thus varies significantly for both olefins*.

* Because of an intrinsic defect of our system of analysis, it has not been possible for us to measure reaction rates for lower 2,3-dimethyl-2-butene concentrations, which would have allowed us a more precise determination of $\beta_{2,3\text{-dimethyl-2-butene}}$.

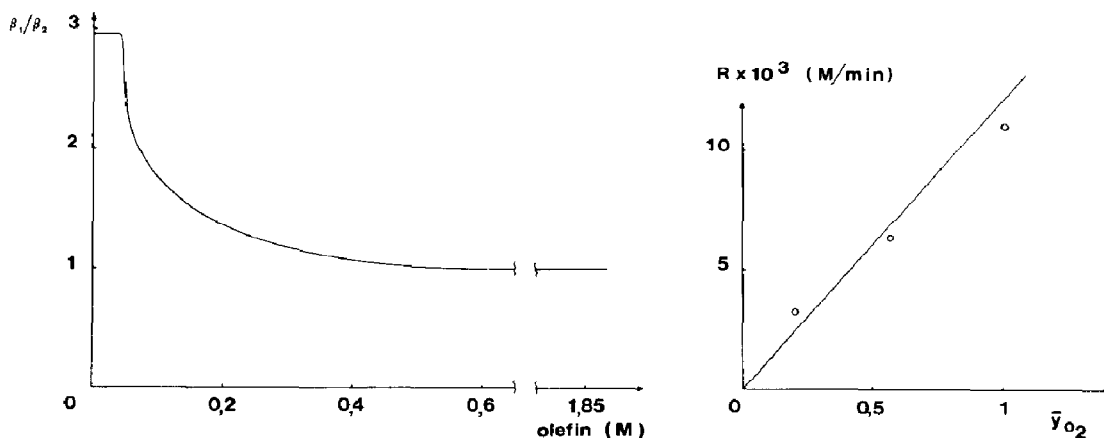


Fig. 4. $\beta_{2\text{-methyl-2-butene}}/\beta_{2,3\text{-dimethyl-2-butene}}$ vs. olefin concentration. Derived directly from the fitting curves of Fig. 2.

Fig. 5. Initial rate vs. oxygen molar fraction in the gas flow \bar{y}_{O_2} . T = room temperature; ethyl alcohol, 260 cm³; methylene blue, 221 mg/l; 2-methyl-2-butene, 0.184 M; gas flux, 150 cm³/min.

The decrease in the reactivity ratio for the two olefins, $\beta_{2\text{-methyl-2-butene}}/\beta_{2,3\text{-dimethyl-2-butene}}$ vs. olefin concentration is reported in Fig. 4. We see that the ratio decreases continuously from 2.9 to 1. These values, calculated on the basis of the fitting lines of Fig. 2, are in contrast with those found in the literature [8, 11 - 13], which report constant values of the ratio ranging from 20 to 50.

In Fig. 5 we report the initial rates obtained by oxidizing the olefin with the same total gas flux, 150 cm³/min, but at various oxygen concentrations, obtained by mixing air and oxygen in different ratios. An approximately linear dependence of the reaction rate on oxygen partial pressure can be deduced.

In Figs. 6 and 7 we report the influence of the total gas phase (pure oxygen) flux on the initial reaction rate. One can observe a sensitive influence of the gas phase flux on the overall reaction rate. Owing to the volatility of the standard olefin employed, it tended to be stripped from the reacting system by the inlet gas at high fluxes. Therefore for fluxes greater than 150 - 200 cm³/min the data obtained are not reliable.

Discussion

Figures 1, 2 and 5 clearly show the dependence of the overall reaction rate on the photosensitizer (methylene blue) and olefin concentration, and on the oxygen partial pressure in the gas phase. In Figs. 1 and 2 we can immediately see that both for high photosensitizer concentration and high olefin concentration the overall reaction rate is concentration independent.

In Fig. 5 we see that the only factor which influences the reaction rate in such a region, to which data of Fig. 5 refer, is the oxygen partial pressure in the gas flux. An empirical rate equation of the form:

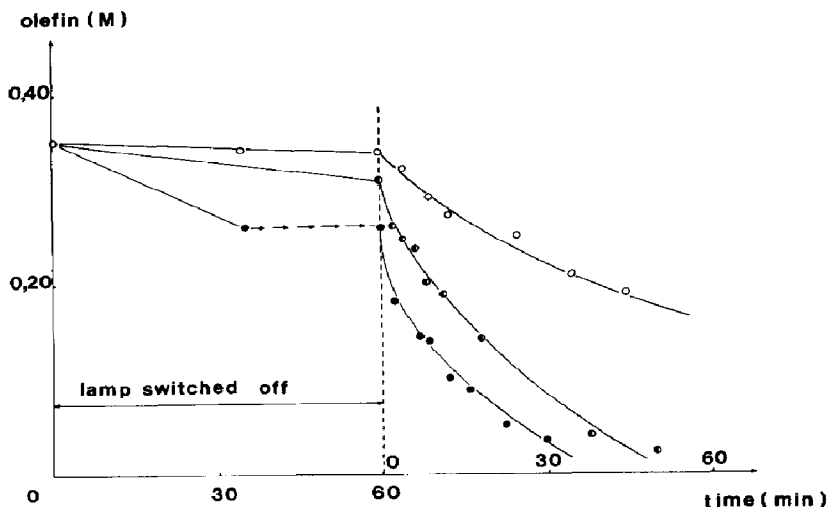


Fig. 6. Olefin disappearance vs. time at different gas (pure oxygen) fluxes. \circ , 40; \square , 150; \circ , 300 cm^3/min . $T = \text{room temperature}$; ethyl alcohol, 260 cm^3/min ; methylene blue, 220 mg/l ; 2-methyl-2-butene, 0.366 M .

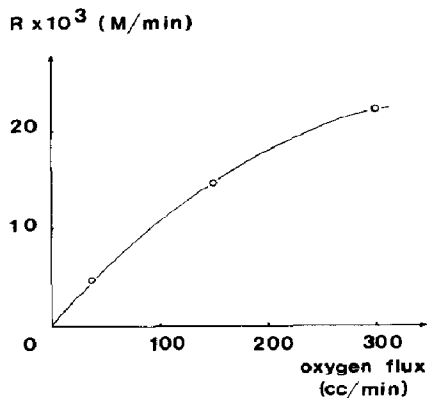


Fig. 7. Initial rate vs. gas (pure oxygen) fluxes. The experimental conditions are those reported in Fig. 6.

$$R = kP_{\text{O}_2}^\alpha$$

where α is approximately equal to 1 fits well the experimental data. In order to analyze this relationship, let us consider the steps which the oxygen undergoes: (1) interphase mass transfer from the gas bubble to the solution, (2) reaction with the irradiated photosensitizer to produce singlet oxygen, (3) chemical reaction of singlet oxygen with the acceptor. Oxygen and singlet diffusion steps have been deliberately omitted from this simplified picture because it is now known that absolute values of the addition rate constant k_2 are some three orders of magnitude lower than the diffusion limited value even for the most reactive acceptors [15, 19].

The data reported in Fig. 2 rule out the kinetic importance of the last step for concentrations higher than 0.40 M . If it were rate determining the

concentration and the type of olefin would have influenced the reaction rate. The reaction rate, however, does not vary with olefin type and concentration in that range.

An interpretation could say that this means that $k_2[A] \gg k_1$, and that thus the chemical reaction rate becomes of zero-order in $[A]$ [3, 10]. However, if we look at the whole concentration range investigated, we see that we go from a region where the reaction rate is concentration dependent to a region at higher concentrations where the reaction rate is not concentration dependent. This change of behaviour occurs in a fairly small concentration range, and thus we do not believe that such a relatively small change in concentration could be responsible for increasing $k_2[A]$ so much with respect to k_1 .

The data reported in Fig. 1 rule out the kinetic importance of the second step as well. In the methylene blue concentration range enquired with two different light intensities we have found a remarkably identical behaviour. In general, a lack of variation of rate with photosensitizer concentration could mean that the quantity of photosensitizer is in excess with respect to the light intensity, and therefore a decrease in photosensitizer concentration is not a decrease in "active" photosensitizer concentration. With two light sources of different intensity, the maximum reaction rate attainable should be different, the quantity of excited photosensitizer being different. In Fig. 1, however, we see that the velocity is the same. Therefore the data in this Fig. should signify that, the concentration of singlet oxygen being independent of the concentration of the excited sensitizer, all dissolved oxygen is excited in a non-rate-determining step and thus the velocity which we have measured is not given by chemical factors.

With regard to the first step, the interphase mass transfer rate is given by [24]:

$$R = K_{Gj} a' P V_b N V_l \left(\bar{y}_j - C_j \frac{H}{P} \right)$$

where R is the mass transfer rate (mol/time), K_{Gj} is the overall mass transfer coefficient (mol/area \times time \times pressure), a' is the ratio of surface area to volume of a single bubble (length⁻¹), V_b is the volume of a single bubble (length³), N is the number of bubbles per unit volume of liquid, V_l is the volume of the liquid phase, other parameters having the usual meaning. If the interphase mass transfer rate were rate controlling, then the overall reaction rate measured experimentally should compare with this equation and behave accordingly. A complete verification of this equation has not been possible so far because of the difficulty in determining, for our reactor, the values of K_{Gj} , a' , V_b and N . Work is in progress to determine them accurately; however, the data we have obtained so far are very illustrative. Actually, as the purely chemical reaction is faster than the interphase mass transfer rate, the oxygen concentration in the solution could be considered negligible; therefore $C_j(H/P) = 0$. Moreover, $K_{Gj} a' V_b N V_l$ could be considered constant (equal to k) when using mixtures of oxygen and nitrogen in different ratios

at the same total gas flux. According to these assumptions the theoretical dependence of R on $\bar{y}P$ would agree with the experimental dependence of the overall reaction rate on the oxygen partial pressure, as shown in Fig. 5.

At high olefin and photosensitizer concentrations considered in the discussion so far, the rate-determining step seems to be the interphase mass transfer of oxygen from the gas phase to the liquid phase. The reaction therefore occurs in a dynamic régime.

Other data in favour of this suggestion are given in Fig. 7, where it is shown that the reaction rate decreases by decreasing the inlet gas flux. Since at $150 \text{ cm}^3/\text{min}$ we are in a dynamic régime, and the same régime is operating at lower fluxes, this can be explained by the decrease in the degree of turbulence inside the reactor and by the decrease in the contact area between the two phases, $a'V_b N$. Oxygen is transferred more slowly to the liquid phase and this slows down the overall reaction rate.

By decreasing the photosensitizer concentration under 0.12 mg/l we decrease the chemical reaction rate, which then becomes the rate-determining step. The same effect is achieved by decreasing the olefin concentration (Fig. 2): first, we enter a transition zone, where the differences in reactivity of the two olefins are slowly enhanced. Under about 0.03 M we are in a purely chemical régime: the rate depends on concentration and on the olefin type.

This change of régimes is evident in Figs. 3 and 4. By plotting $1/[AO_2]$ against $1/[A]$ at low acceptor concentrations (Fig. 3a) we have obtained straight lines, in accordance with the theoretical rate equation described in the introduction. The values of β were thus calculated as ratios of slope, $\beta/I_a \Phi_{1O_2}$, to intercept, $1/I_a \cdot \Phi_{1O_2}$:

$$\beta_{2\text{-methyl-2-butene}} = 1.65 (M)$$

$$\beta_{2,3\text{-methyl-2-butene}} = 0.56 (M)$$

As the concentrations increase, the interpolating lines are no longer straight and they become a single curve for high concentrations. In such a situation the values of β lose their chemical significance and the presence of a dynamic régime is evident.

The ratio $\beta_{2\text{-methyl-2-butene}}/\beta_{2,3\text{-dimethyl-2-butene}}$ obtained from the interpolating curves of Fig. 2 is plotted in Fig. 4. We can see that this ratio is constant at low olefin concentrations; then it gradually decreases to become equal to one at high concentrations. This is a clear demonstration of the presence of the two régimes and of the intermediate transition zone.

Conclusions

In this paper we have pointed out that when investigating the kinetics of a dye-sensitized photo-oxygenation of 2-methyl-2-butene and 2,3-dimethyl-2-butene with a gas-liquid photoreactor, it is possible to have two different régimes in which the reaction occurs: (1) a dynamic régime at olefin concentrations higher than 0.40 M and at sensitizer concentrations higher than

12 mg/l; (2) a chemical régime at olefin concentrations lower than 0.03 M and at sensitizer concentrations lower than 10 mg/l.

An empirical kinetic equation $R = kP_{O_2}^\alpha$ with α approximately equal to one has been found to represent the dynamic régime.

The value of $\beta_{2,3\text{-dimethyl-2-butene}} = 0.56$ and the value of $\beta_{2\text{-methyl-2-butene}} = 1.65$ have been determined in the chemical régime.

We have seen that outside the chemical régime range the ratio of these two β varies continuously from 2.9 to 1; this variation clearly depicts the presence of the chemical, intermediate and dynamic régimes.

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