KINETIC STUDIES OF KITON RED S PHOTODECOMPOSITION UNDER CONTINUOUS WORKING AND FLASH PHOTOLYTIC CONDITIONS

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Summary

Dilute solutions of Kiton Red S (10^{-4} - 10^{-3} M) in ethanol were subjected to photolysis under continuous working (CW) and flash photolytic conditions. The rate expression for degradation of this xanthene dye was determined by means of quantitative IR analysis.

Under CW conditions it was found that the rate was independent of the dye concentration, but was dependent on the concentration of oxygen dissolved in solution. The rate of degradation was accelerated by oxygen. It is suggested that, under these conditions, a molecular form of oxygen is the agent responsible for dye degradation.

Under flashed conditions the rate of dye degradation was again found to be independent of dye concentration. In this case the oxygen acted as an inhibitor of the degradation process. Also it was discovered that, when light of wavelength less than 240 nm was filtered out, no dye decomposition occurred. In this case it is suggested that, under the influence of light of wavelength shorter than 240 nm, the oxygen is dissociated into atomic oxygen which is the agent responsible for degradation. However, solvent excitation is also a factor under these conditions.

1. Introduction

The xanthene dyes have been used extensively in the cavities of flash-lamp-pumped lasers [1]. It is known that these dyes photobleach when they are subjected to continuous working (CW) [2], flash lamp [3] or laser irradiation [4] conditions. This photobleaching leads to loss of lasing power and ultimate quenching of the beam. There is evidence from other dye systems [5] which suggests that the decrease in lasing power and the final stoppage of lasing is caused by degradation of the dye. Verification of this finding was sought, as well as the elucidation of the factors associated with the degradation which were responsible for the decreased laser output.

Kiton Red S (the sodium salt of sulforhodamine B) [6] was the xanthene dye selected for use in this study. Kiton Red S (KRS) is an efficient laser dye over the range 589 - 642 nm [1], and has demonstrated both long lasing lifetimes and efficiencies up to 1.4% in a coaxial flash-lamp-pumped laser operated in a single-pulse mode [7].

Many xanthene dyes have been shown to have high thermal stability in solution [8]. It can be concluded from this observation that the ground states of these dyes are quite stable.

Extensive fragmentation occurs during degradation of KRS. Using thin layer chromatography, Dorko *et al.* [9] have been able to isolate from a degraded solution at least five different compounds with significantly different structures.

There are reports of more than one reaction path occurring simultaneously in the degradation of various dyes [5, 10]. It has been suggested that the solvent is an integral part of the reaction mechanism [10 - 12]. The photochemical reaction products also play a significant role in the degradation process [10]. Finally, oxygen dissolved in the dye solution exerts significant effects on the degradation. Molecular oxygen has long been known to be an effective quencher of undesirable triplet states [3, 13, 14]. Also upon photodissociation, oxygen can act as an oxidizing agent and thus can participate in the dye solution degradation reaction. Molecular oxygen photodissociates to atomic oxygen under the influence of light of wavelength below 240 nm [15, 16].

The observed effects of oxygen in a degrading dye solution have been remarkably varied. Beer and Weber [17] have shown that oxygen increases the bleaching rate for rhodamine 6G in methanol during irradiation by a continuous argon laser, whilst Kato and Sugimura [10] have found that, under exposure to UV light from a low pressure mercury–argon lamp, the degradation is inhibited by oxygen. Schwerzel and Edie [18] have shown that oxygen slows the degradation rate of a KRS–methanol solution during illumination by a medium pressure mercury arc lamp.

Johnson [7] has demonstrated that the photodegradation rate for KRS in various solvents is slowed if the triplet quencher cyclooctatetraene is added to the dye solution. Yamashita and Kashiwagi [11], after directly detecting a decrease of T_1 molecules and an increase of free radicals during degradation, have concluded that a chemical reaction between the triplet dye molecules and the solvent leads to photodegradation of various xanthene dyes in ethanol.

2. Experimental

2.1. Materials used

Kiton Red S was purchased as Kiton Red 620 from the Exiton Co., Dayton, Ohio. Thin layer chromatography and nuclear magnetic resonance analysis showed the material to be free of organic impurities. Dehydrated

analyzed reagent grade ethanol from U.S. Industrial Chemicals Co. was used as solvent.

2.2. CW irradiation

A conventional photolysis system consisting of a light source, a quartz reaction vessel for the dye solution and a gas source was used. A 200 W Osram HBO 200 mercury point source was used as the light source. Its spectrum consists of a series of narrow bands ranging from about 270 nm to 600 nm [19]. The lamp was housed in a Bausch and Lomb housing and was powered by an Oriel 8500 power supply. The light beam passed out of the housing and through a quartz condenser lens system into a 100 ml quartz reaction vessel.

Gas was passed into the reaction vessel through a glass fit. After passage through the dye solution, the gas stream was vented to the atmosphere through a bubbler system. Aliquots for analysis were removed from the reaction vessel by means of a gas-tight syringe through a rubber septum attached to a side arm of the vessel. A water-cooled reflux condenser was used to keep solvent in the vessel.

The general procedure for performing the CW photolysis experiments was as follows. Approximately 75 ml of 10^{-3} M KRS in ethanol was placed into the reaction vessel. Gas was bubbled through the dye solution for 2 h prior to irradiation. Aliquots of 1 ml were withdrawn for analysis at 12 h intervals.

2.3. Flash photolysis in a laser cavity

The laser system used in this work was a Phase-R DL 1100 flash-lamp-pumped laser with a triaxial cavity configuration. In this configuration there is an annular space between the dye cavity and the flash lamp through which a coolant can flow. This annular region can be effectively used to filter the flash lamp radiation by the insertion of a filter fluid.

The laser head consisted of the DL 10 xenon flash lamp with a triaxial adaptor. The flash lamp was annular in shape with an inner diameter of 10 mm and a length of 140 mm. The flash lamp produced a spectrum comparable with a black body at 25 000 K, and the average pulse was of the order of 500 ns [20]. The cylindrical quartz tube making up the dye cavity was 250 mm in length and had a 6 mm inner diameter. The annular sleeve around the dye cavity (the filter fluid cavity) was 1 mm thick and extended along the entire length of the dye cavity. The power supply and the controls were standard DL 1100 equipment.

In each experiment a selected gas was bubbled into the dye solution. The gas was fed into the circulating dye through a capillary inserted into the line. The general procedure for performing the flash photolysis experiments was as follows. The dye reservoir was filled with 500 ml of 2×10^{-4} M KRS solution and the filter fluid reservoir was filled with 500 ml of the appropriate filter fluid. Gas was bubbled into the circulating dye solution for 2 h prior to flashing in order to permit equilibration of the dissolved gas in the dye

solution. The voltage across the capacitor bank immediately before pulsing the flash lamp was 18 kV and the repetition rate was approximately 40 shots min^{-1}.

For analysis, 2 ml samples of the dye solution were withdrawn with a syringe just prior to flashing and at appropriate intervals after flashing commenced. The laser beam energy was measured at the beginning of lasing. Energy readings were also taken each time a sample was withdrawn. The measurements were made with a Quantronix 504 energy power meter with an attached 501 energy receiver.

2.4. Quantitative analysis using the IR spectrum

A 0.150 g sample of oven-dried KBr was placed into a stainless steel capsule along with 1.0 cm^3 of the dye solution which had been withdrawn during a photolysis experiment. The solvent was evaporated under reduced pressure. The dry mixture was shaken for 1 min on an amalgam shaker. A 0.1 g portion of the homogeneous mixture was made into a KBr pellet in the usual manner. The IR spectrum was obtained using a Perkin–Elmer 137B spectrophotometer. A spectrum of pure KRS is shown in Fig. 1(a). For comparison the spectrum of the non-volatile decomposition product mixture is shown in Fig. 1(b). At 7.50 μm the product mixture spectrum shows no
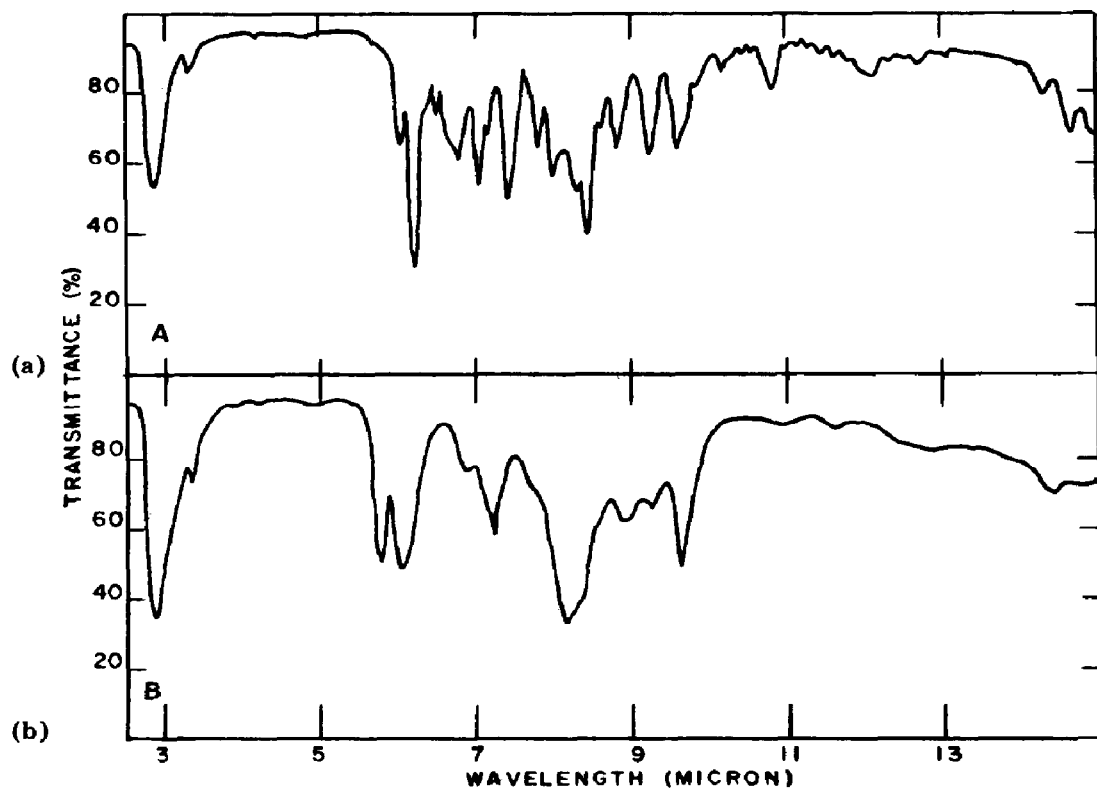

Fig. 1. IR spectra: (a) Kiton Red S; (b) non-volatile decomposition products.

absorption, whereas KRS shows a band of medium intensity. This band was used for the quantitative IR analysis of KRS. Since other bands in the region prevent a return of the 7.5 μm band to the baseline, the modified approach developed by Fritz and Hammond [21] (which uses a tie-line) was employed for the analysis. A calibration curve was prepared using this technique. A correlation coefficient of 0.99, obtained from a least-squares analysis of the data points, indicates that the Beer—Lambert Law is valid over the concentration range of interest. The rate at which the concentration of KRS decreased during the photodegradation experiments was measured by quantitative analysis of the IR spectrum.

2.5. UV analysis of the filter fluids

UV spectra were obtained for each of the three filter fluids (deionized water, ethanol and ethyl acetate) used in the flash photolysis studies, in order to determine the wavelength cutoff of each. The wavelength cutoff point for a particular filter fluid is defined as that wavelength below which the transmittance is less than 5%. A UV spectrum of deionized water showed 100% transmittance down to 185 nm, the lower limit of the spectrophotometer. Spectra of ethanol and ethyl acetate showed cutoff wavelengths of 192 and 244 nm respectively. Also, a UV spectrum was obtained of the ethanol filter fluid after 5000 flash lamp pulses.

3. Results

3.1. CW photolysis

A typical plot of KRS concentration *versus* time is shown in Fig. 2. It shows the decrease of KRS concentration with time during CW photolysis when a gas mixture of 10.3% O_2 and 89.7% Ar was bubbled through the solution during irradiation. The plot is linear. A least-squares analysis of the data gave a correlation coefficient of 0.97. Similar plots for irradiation with 21% O_2 and with pure argon bubbling through the solution also showed linearity. The linearity of the concentration decay indicates that the reaction is zero order in KRS concentration.

Based on the results obtained from such plots, the apparent zero order rate constant k_{app} was calculated for the three conditions studied. The calculated results are given in Table 1.

The rate constant appears to be a function of oxygen concentration. Based on the results of the studies with 10.3% and 21% O_2, the oxygen dependence and the concentration-independent zero order rate constant k could be obtained from

$$k_{app} = k[O_2]^a \qquad (1)$$

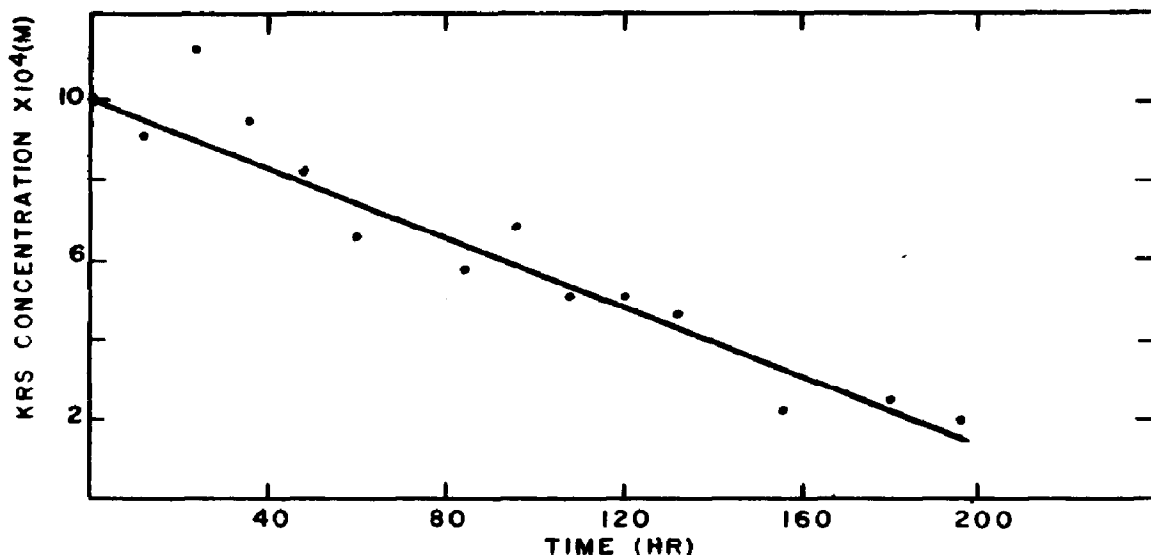where k_{app} is the apparent rate constant and a is the oxygen concentration power dependence.

Fig. 2. A plot of the KRS concentration, obtained by IR analysis at 7.5 μm, *vs.* time during the CW irradiation of the dye solution with a 10.3% O_2–89.7% Ar gas mixture bubbled through the solution.

TABLE 1

Numerical results of kinetic studies under CW photolysis conditions

Oxygen in gas mixture (%)	Concentration of dissolved oxygen[a] (mol l^{-1})	Apparent rate constant k_{app} (mol l^{-1} s^{-1})
0[b]	0	1.8×10^{-10}
10.3[c]	1.0×10^{-3}	1.3×10^{-9}
21[d]	2.1×10^{-3}	1.5×10^{-9}

[a] Calculated using Henry's law [22].
[b] High purity argon (99.995%).
[c] A mixture of 10.3% O_2 and 89.7% Ar.
[d] Breathing air.

The concentration of oxygen in solution was calculated using Henry's law. The data and method employed to obtain Henry's law constant are reported in ref. 22. The value of the constant was calculated to be 1.3 × 10^6 mmHg at 20 °C for pure ethanol solvent.

The value of the concentration-independent zero order rate constant calculated using this procedure is 4.3 × 10^{-9} (mol l^{-1})$^{0.83}$ s^{-1}. The calculated value of *a* is +0.17.

3.2. Flash photolysis

A typical plot of KRS concentration *versus* shot number under flash photolytic conditions is shown in Fig. 3. A plot of the decay of the laser
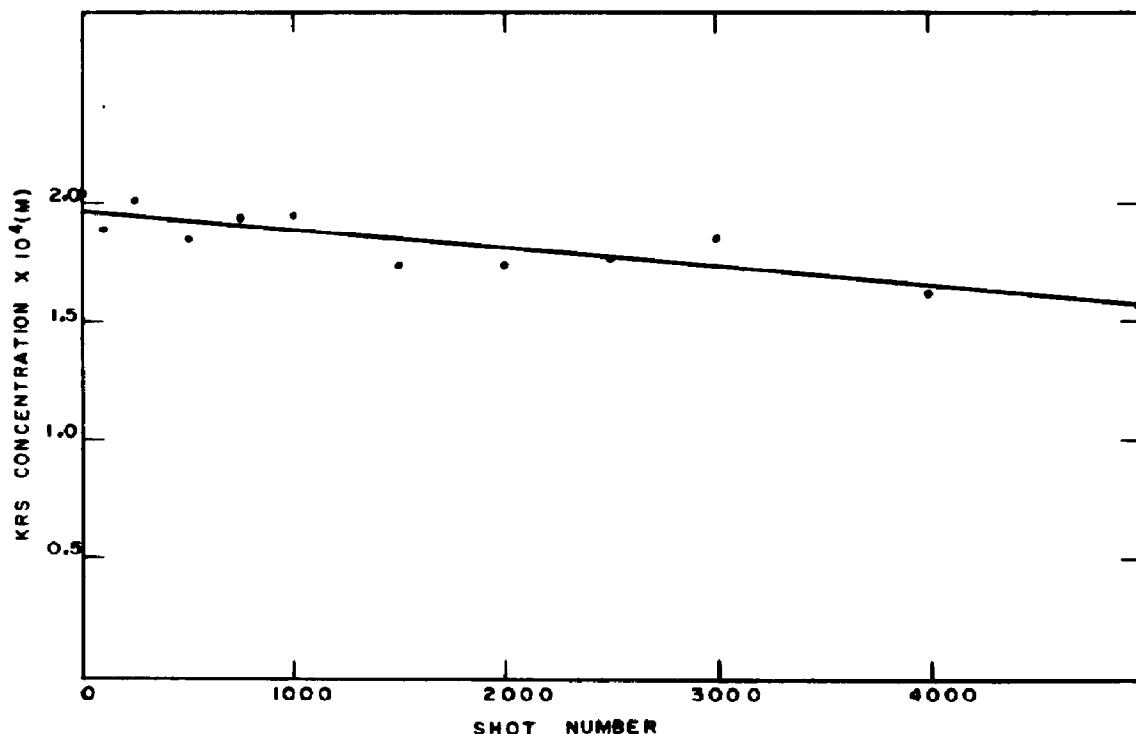
Fig. 3. A plot of the KRS concentration, obtained by IR analysis at 7.5 μm, vs. shot number during flash photolysis of a 2 × 10^{-4} M dye solution with a 10.3% O_2–89.7% Ar gas mixture bubbled through the solution and deionized water used as filter fluid.

beam energy *versus* shot number is shown in Fig. 4. These plots are for a 2 × 10^{-4} M dye solution through which a mixture of 10.3% O_2–89.7% Ar was bubbled. Deionized water was used as the filter fluid.

The decrease in KRS concentration with shot number is linear. A least-squares analysis of the data gave a correlation coefficient of 0.86. All data from additional similar experiments produced linear plots of KRS concentration *versus* shot number. The results from these experiments are listed in Table 2. Again the KRS decay is zero order in KRS concentration. The laser beam energy decays exponentially. This decay pattern for the laser beam energy is well documented for the xanthene dyes [7]. Dye and beam half-lives were obtained from the plots and these values are reported for all the experiments.

Using the results obtained with the experiments listed as trials 1, 2 and 3, the apparent rate constant for dye degradation was calculated. The results are shown in Table 3. From these data the concentration-independent zero order rate constant was calculated with eqn. 1 to be 2.8 × 10^{-9} (mol l^{-1})$^{1.15}$ shot^{-1} and the oxygen concentration power dependence was calculated to be −0.15.
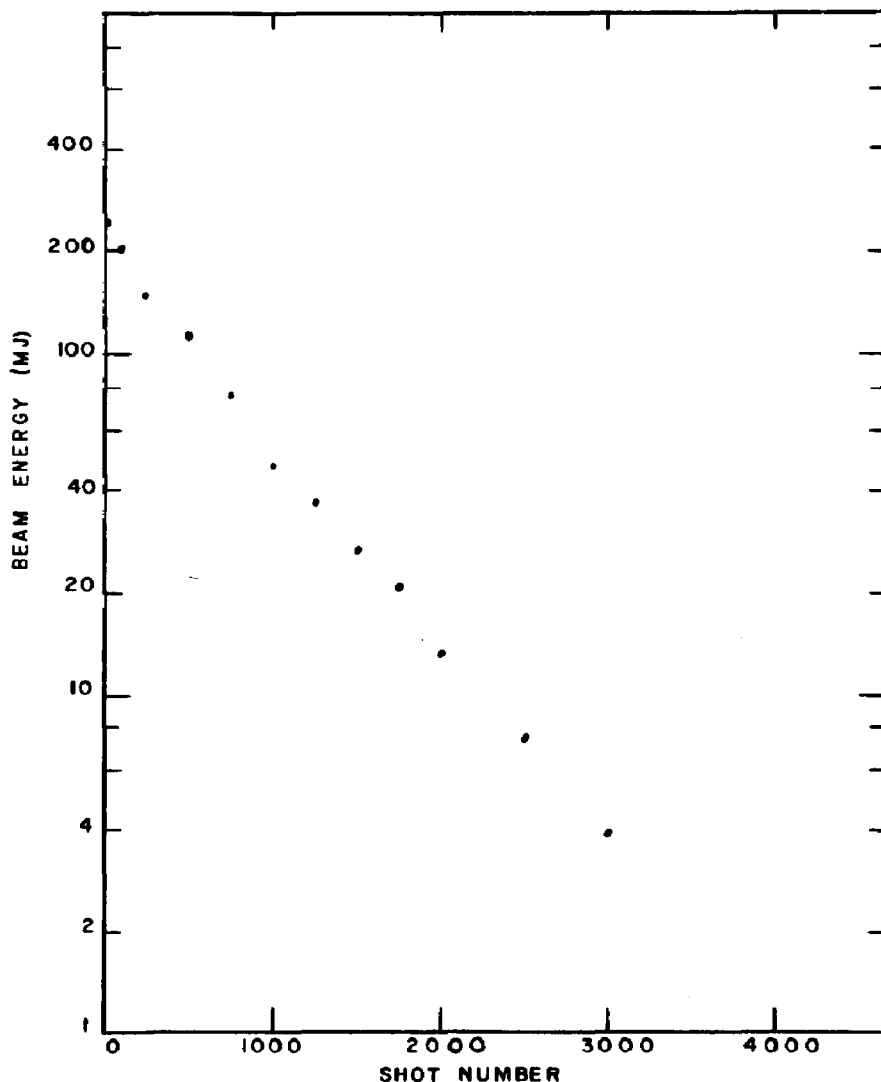
Fig. 4. A plot of the decrease in laser beam energy *vs.* shot number during flash photolysis of a 2×10^{-4} M dye solution with a 10.3% O_2–89.7% Ar gas mixture bubbled through the solution and deionized water used as filter fluid.

4. Discussion

4.1. *CW photolysis*

The positive value of the oxygen concentration dependence of the degradation of KRS shows that, under these conditions, oxygen acts to aid the degradation. However, since the rate expression is zero order in KRS concentration, the rate of degradation is not a function of dye concentration. These two results suggest that, if the dye is a factor in its own decomposition, its influence is in the role of catalyst.

TABLE 2

Experimental results of flash photolysis experiments

Trial	Filter fluid	Gas mixture	Initial beam energy (mJ)	Laser half-life (no. shots)	KRS concentration half-life[a] (no. shots)
1	H_2O	Ar[b]	250	550	7 400
2	H_2O	10.3% O_2[c]	230	500	12 700
3	H_2O	21% O_2[d]	200	450	14 300
4	Ethanol	Ar[b]	220	3 000	900 000
5	Ethanol	21% O_2[d]	180	750	35 200
6	Ethyl acetate	21% O_2[d]	92	8 500	∞

[a] A quantitative IR technique was used to obtain the KRS concentration.
[b] High purity argon (99.995%).
[c] 10.3% O_2–89.7% Ar.
[d] Breathing air.

TABLE 3

Numerical results of kinetic studies under flash photolysis conditions

Trial	Oxygen in gas mixture (%)	Concentration of dissolved oxygen[a] (mol l^{-1})	Apparent rate constant k_{app} (mol l^{-1} shot^{-1})
1	0[b]	0	1.3×10^{-8}
2	10.3[c]	1.0×10^{-3}	7.8×10^{-9}
3	21[d]	2.1×10^{-3}	7.0×10^{-9}

[a] Calculated using Henry's law [22].
[b] High purity argon (99.995%).
[c] A mixture of 10.3% O_2 and 89.7% Ar.
[d] Breathing air.

4.2. Flash photolysis

The degradation of KRS under flash photolytic conditions is again zero order in KRS concentration. However, on a time scale basis and from the experiments with unfiltered light, the half-life of the degradation process under flash photolysis is of the order of milliseconds. This observation is in sharp contrast with the half-life measured in hours or days for CW photolysis.

Based on the KRS degradation curve of Fig. 3 and the laser beam energy decay curve of Fig. 4, it is apparent that a multiplier effect is operating. The degradation of KRS follows a linear decay path whilst the degradation of laser beam energy is exponential. The same effect was noted in all the trials reported in Table 2. A comparison of the corresponding half-lives indicates that this observation is consistent. This correspondence between a complete

loss of laser energy and a comparatively small loss in dye concentration seems to indicate that the energy output is not a function of dye concentration alone. Apparently the photoreaction products are competing for the laser radiation or the pump energy or both.

Oxygen played an important role in both beam energy degradation and dye degradation. It is clear from Table 2 that, for either a water or an ethanol filter fluid, the presence of oxygen in solution acts to shorten the lasing half-life. With an ethyl acetate filter fluid, laser energy degradation virtually ceased. The effect of oxygen on the dye degradation rate, however, was markedly dependent on the specific filter fluid used. When the full spectral range of the flash lamp was allowed to excite the dye solution (trials 1 - 3), the presence of oxygen in solution inhibited the rate of dye degradation. The results of the kinetic analysis reported in Table 3 quantify the inhibiting effect of oxygen for the case of unfiltered light. However, when wavelengths below 192 nm were eliminated from the dye cavity, the effect of oxygen was to accelerate the rate; when radiation below 244 nm was excluded, no decomposition at all occurred.

4.3. General discussion

Using the data obtained under flash photolytic conditions, the following observations can be made. When oxygen is present in solution and wavelengths less than 244 nm are allowed to excite the dye solution, molecular oxygen which is dissolved in solution is dissociated into atomic oxygen. Molecular oxygen has an allowed transition $B^3\Sigma_u^- - X^3\Sigma_g^-$ which results in photodissociation [15, 16]. This allowed transition produces the well-known Schumann–Runge bands in the UV [23]. The absorption begins at approximately 240 nm [15] and extends to 175.9 nm [23]. This atomic oxygen species then oxidizes the solvent to form free radicals which lead to products that absorb laser radiation or flash lamp (pump) radiation. The rate of formation of these radicals, which are designated R_1, is dependent on the concentration of oxygen and on the excitation energy. By increasing the amount of dissolved oxygen or the energy of excitation, the laser half-life is shortened. This accounts for the exceptionally long half-life demonstrated in the sixth trial, where wavelengths shorter than 244 nm were obstructed. In this trial oxygen in solution was unable to dissociate and act as an oxidant.

These R_1 radicals are similar to those found by Mostovnikov et al. [12], who have reported that flash lamp irradiation of the solvent alone (before mixing with the dye) has the same effect on the lasing efficiency of rhodamine 6G as irradiating the dye and solvent together. The presence of these radicals is also arguable in the light of the conclusion of Winters et al. [5] that it is the presence of oxygen which leads to the production of laser-inhibiting substances in coumarin dyes.

There is a group of wavelengths shorter than 192 nm which induces free radical formation in the solvent. It is well known that, at wavelengths between 180 and 190 nm, the $n \rightarrow \sigma^*$ transition occurs in alcohols [24]. This transition may be the initial step in the pathway for radical formation.

These radicals, designated R_2, are different from the R_1 radicals discussed earlier in that they react with the triplet dye molecules to form fragments. However, they preferentially react with molecular oxygen (over their rate of interaction with the dye) to create harmless intermediates not capable of reaction. Therefore as the amount of oxygen is increased, the degradation rate slows down. In cases where no oxygen is available (as in trial 1 of Table 2), the rate is accelerated as these R_2 radicals become available to react with the prevalent dye triplets. Two reports are consistent with this conclusion. Schwerzel and Edie [18] have found that, for oxygen-saturated solutions of KRS in methanol, the degradation rate is rapidly accelerated after the oxygen in solution has been expended. Kato and Sugimura [10] have observed a similar effect with a solution of rhodamine 6G in methanol; they have further observed that, after the rate has accelerated, a fresh supply of oxygen acts to slow the rate again.

If wavelengths less than 192 nm are not permitted to excite the dye solution, R_2 radicals are not formed and oxygen alone influences the rate of degradation. The explanation is as follows. With light of sufficient energy to dissociate molecular oxygen, its rate as oxidizer of the triplet dye molecules becomes more significant than its quenching rate. Under these conditions more oxygen in solution leads to accelerated dye degradation rates. When wavelengths less than 244 nm are excluded from the dye solution, however, molecular oxygen remains intact and its triplet quenching rate dominates. The dye then does not degrade, as evidenced by the sixth trial of Table 2.

During CW irradiation a somewhat different situation prevails. The irradiation was accomplished by an Osram HBO 200 lamp whose spectral region extends down only to 240 nm [19]. The decomposition under these conditions is very slow, taking place over a period of several days. It is postulated that, under these conditions, a more conventional dye-sensitized oxidation of the dye is occurring. For example, it is well known that anthracene and other polynuclear hydrocarbons form peroxides with molecular oxygen during irradiation by UV light [25]. Further, these peroxides or the singlet oxygen which is postulated to form from them have been shown to oxidize effectively compounds containing double bonds including other molecules of the starting polynuclear hydrocarbon. It has been shown that the dianions of fluorescein and of its derivatives can form such adducts or peroxides [26]. The fluorescein dianion has the xanthene structure. There is a striking resemblance between this molecule and KRS. Under such circumstances it is reasonable to postulate that this type of oxidation of KRS is occurring under CW photolysis since the wavelengths which initiate these reactions occur at 365 nm or longer [27]. Under CW conditions, light in the wavelength region 240 - 600 nm was used for irradiation of the KRS solution.

This type of oxidation may also be occurring during the flash photolytic irradiation of KRS. However, based upon the results of trial 6 (Table 2), if it is occurring it seems that its rate is quite slow compared with that of the other processes which are postulated.

Acknowledgments

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