

# $H_2O_2$ /UV degradation kinetics of isoprene in aqueous solution

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## Abstract

Hydrogen peroxide and UV radiation have been used in the photochemical degradation of isoprene in aqueous solutions. A kinetic study is carried out taking into account the contribution of the UV radiation reaction and the combined reaction with hydrogen peroxide. An empirical reaction rate expression, which considers the two reactions taking place in parallel, is suggested. Pseudo-first order rate constants are obtained from batch reactor data. As the molar ratio of  $H_2O_2$ :isoprene increases, the rate of reaction increases linearly while the concentration of  $H_2O_2$  is observed to be nearly constant throughout the reaction; suggesting that the  $H_2O_2$  acts as a pseudo-catalyst. Nearly complete oxidation of isoprene is achieved. These results indicate that the  $H_2O_2$ /UV process appears to be a competitive alternative destructive treatment for removing isoprene from water present at low levels. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Pseudo-catalytic oxidation; UV; Hydrogen peroxide; Isoprene; Kinetics

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## 1. Introduction

Toxic and hazardous VOCs are often present in industrial wastewater and water supplies. Removal of these compounds may be difficult and costly if present in relatively small concentrations. Conventional treatment processes, such as air stripping, activated carbon adsorption, and biological treatment, although quite effective in certain water treatments has some limitations. Adsorption and air stripping merely transfer the contaminants from one environmental medium to another, e.g. from water to air or carbon, while biological treatment generates a waste that may require further treatment.

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More recently, various studies concerning the chemical oxidation of VOCs present in aqueous systems using hydroxyl radicals to carry out the oxidation reaction have been reviewed [1]. Hydroxyl radicals are generated by the combination of UV radiation and hydrogen peroxide and/or ozone. This oxidation process is an attractive treatment method because of its high efficiency and simplicity in destroying the contaminants leaving no residue. The oxidation products are usually low molecular weight oxygenated compounds that are easily biodegradable or, in some instances, the organic compound reduces to carbon dioxide and water.

Isoprene, the monomeric unit of natural rubber and naturally occurring terpenes and steroids, is produced and emitted from certain plants and trees [2]. Natural rubber has about 4000 isoprene units arranged in a straight chain. Isoprene is of particular interest to atmospheric chemists because it participates in a suite of tropospheric reactions that reduce the oxidative capacity of the atmosphere [3]. The kinetics of these reactions were measured in environmental chambers that simulate photochemical smog reactions that take place in the atmosphere [4,5]. Extensive chemical mechanisms for isoprene photooxidation have been developed to represent its atmospheric reactions [6–8].

This paper presents the kinetics of the oxidation of the reactions of isoprene in aqueous solutions, catalyzed by  $\text{H}_2\text{O}_2$  and UV radiation. Isoprene, being a pollutant in natural rubber processing wastewater, for which, to our knowledge, there is no reported kinetic data of its UV/ $\text{H}_2\text{O}_2$  oxidation in the aqueous phase.

## 2. Experimental methods

The experiments were conducted in a 250-ml batch photo reactor provided with a magnetic stirring device as shown schematically in Fig. 1. A low-pressure ultraviolet lamp was mounted at the top of the reactor. The lamp had a relative maximum intensity at 254 nm and at a distance of 75 mm of  $2250 \mu\text{w}/\text{cm}^2$ . The depth of the liquid in the reactor was kept constant at 3 cm. The distance from the bottom of the reactor was kept close to 3 cm to insure maximum penetration of light. For every experiment conducted, the reactor was charged with the aqueous solution of isoprene and hydrogen peroxide in

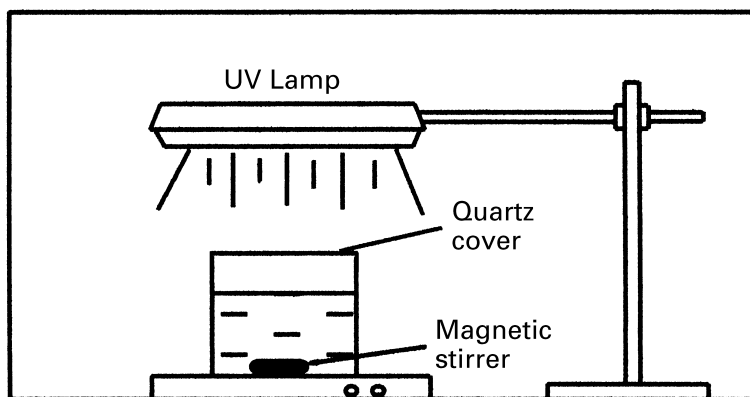


Fig. 1. Schematic diagram of the batch photoreactor.

predetermined concentrations. Isoprene initial concentration was kept constant at 1.47 mM while the molar ratio of hydrogen peroxide: isoprene was varied from 0–6. The temperature and pH of the reaction mixture were measured as a record of the experiment and kept constants at 24°C and 6.8, respectively. Once the lamp was switched on, a stop-watch was started to record reaction time and typical reaction runs lasted 60 to 180 min. The light intensity was kept constant at its maximum value in all experiments. At regular intervals, samples were withdrawn for analysis of isoprene using a double beam UV-VIS spectrophotometer (Varian Optical Spectroscopy Instruments Model Cary 300 Version 6.01). Hydrogen peroxide was determined by a glucose oxidase–peroxidase method [9]. Samples from a few runs of the isoprene reaction were extracted into ethyl acetate, acidified, dried and analyzed for reaction intermediates by GC/MS (Hewlett Packard Model HP 589).

Isoprene (Merck > 98%) and hydrogen peroxide (30% aqueous) were used as supplied.

### 3. Results and discussion

The degradation of isoprene in dilute aqueous solutions by UV and by combined  $\text{H}_2\text{O}_2$  and UV radiation was studied at constant temperature, pH, initial concentrations of isoprene and variable  $\text{H}_2\text{O}_2$  concentrations. Fig. 2 shows the conversion of isoprene against time for various  $\text{H}_2\text{O}_2$ :isoprene ratio ( $R$ ). With UV alone, a slower rate of reaction was observed. The combination of  $\text{H}_2\text{O}_2$  and UV radiation was more effective than UV alone in destroying isoprene. Isoprene is attacked by UV photons and by hydroxyl radicals generated from the photolysis of  $\text{H}_2\text{O}_2$ . As the molar ratio of

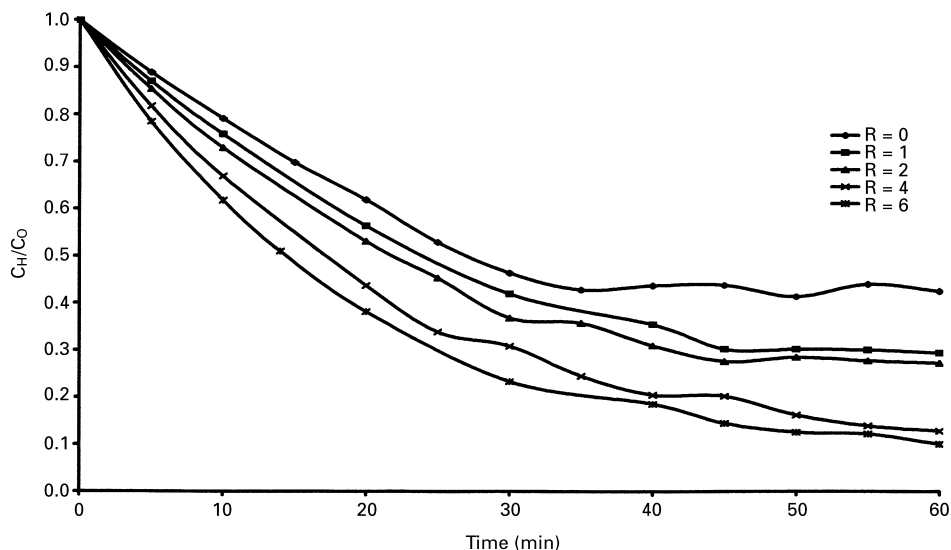
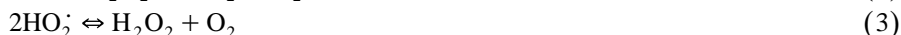


Fig. 2. Effect of hydrogen peroxide:isoprene molar ratio on reaction.

hydrogen peroxide to isoprene was increased, more hydroxyl radicals were available and the rate of reaction was increased. Several investigators [10–14] have studied the effect of  $\text{H}_2\text{O}_2$  concentration in the photo-degradation of organic compounds in aqueous solutions. They found out that the concentration of  $\text{H}_2\text{O}_2$  decreased slightly or remained essentially constant with reaction time. This result was also observed in this study, as shown in Fig. 3 for different  $\text{H}_2\text{O}_2$ :isoprene molar ratios. This observation may be explained by taking into account the mechanisms suggested for the photochemical decomposition of  $\text{H}_2\text{O}_2$  [15]:



where  $\nu$  is the frequency of radiation ( $\text{s}^{-1}$ ) and  $h$  is Planck's constant, J s.

Or more importantly, the complex mechanisms suggested by several authors [1,10,16–20] that can be simplified by following the path leading to the regeneration of  $\text{H}_2\text{O}_2$ :



The simplified paths of Eq. (4) show the cleavage of the  $\text{H}_2\text{O}_2$  molecule into hydroxyl radicals by the absorption of UV radiation. These highly reactive radicals react with the

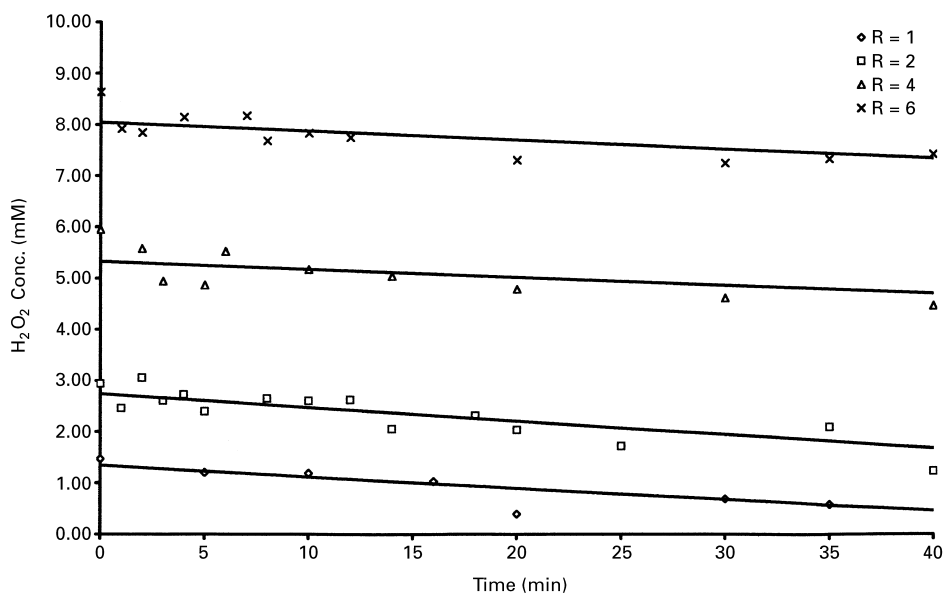


Fig. 3. Variation of hydrogen peroxide concentration during reaction.

organic compounds HRH yielding the final products of oxidation and at the same time regenerating  $\text{H}_2\text{O}_2$ . The reaction of hydroxyl radicals and hydroperoxyl radicals also produces  $\text{H}_2\text{O}_2$ . This complex decomposition–formation of  $\text{H}_2\text{O}_2$  is responsible for the observed nearly constant concentration of  $\text{H}_2\text{O}_2$  during the UV/ $\text{H}_2\text{O}_2$  reactions of VOCs. Thus, the photo-degradation of isoprene in aqueous solutions could be described by two reactions taking place in parallel; a purely photolysis reaction and a  $\text{H}_2\text{O}_2$  pseudo-catalyzed reaction. The overall reaction rate expression would then be the addition of the contributions of these two reactions and may be postulated as follows:

$$(-r_{\text{H}}) = -\text{d}C_{\text{H}}/\text{d}t = k_1 C_{\text{H}}^a I^b + k_2 C_{\text{H}}^c C_{\text{p}}^d I^e \quad (5)$$

where  $r_{\text{H}}$  = reaction rate w.r.t. hydrocarbon H ( $\text{mol}/\text{cm}^3 \text{ s}$ );  $C_{\text{H}}$  = concentration of H (mM);  $k_1$  = rate constant with UV radiation only;  $I$  = UV radiation intensity ( $\text{kW}/\text{m}^2$ );  $k_2$  = rate constant with both  $\text{H}_2\text{O}_2$  and UV radiation;  $C_{\text{p}}$  = concentration of  $\text{H}_2\text{O}_2$  (mM); and a, b, c, d, and e are reaction orders.

The UV radiation intensity was kept constant in all the experiments performed. In addition, it was shown that  $\text{H}_2\text{O}_2$  concentration during the course of all the experiments was constant and that it played the role of a catalyst in the UV/ $\text{H}_2\text{O}_2$  reaction. With these considerations, and the fact that the catalyst does not change the order of the reaction, Eq. (5) may be written as:

$$(-r_{\text{H}}) = (k_3 + k_4) C_{\text{H}}^n \quad (6)$$

where  $k_3 = k_1 I^b$  and  $k_4 = k_2 I^e C_{\text{p}}^d$ ,  $n$  is reaction order.

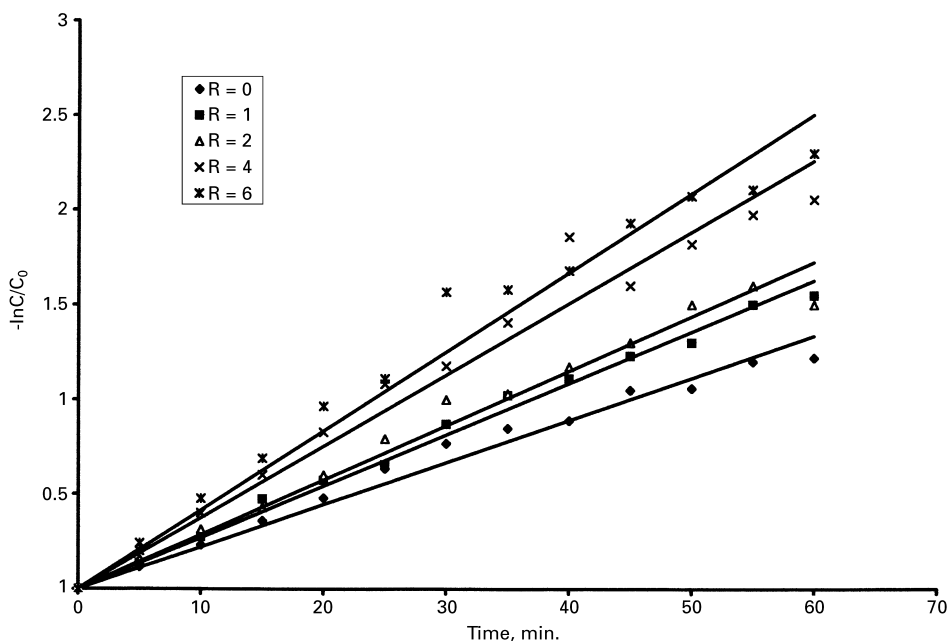


Fig. 4. Determination of the rate constants  $(k_3 + k_4)$  and  $k_3$ .

Table 1

Pseudo-first order rate constants for isoprene by UV alone and UV/H<sub>2</sub>O<sub>2</sub>

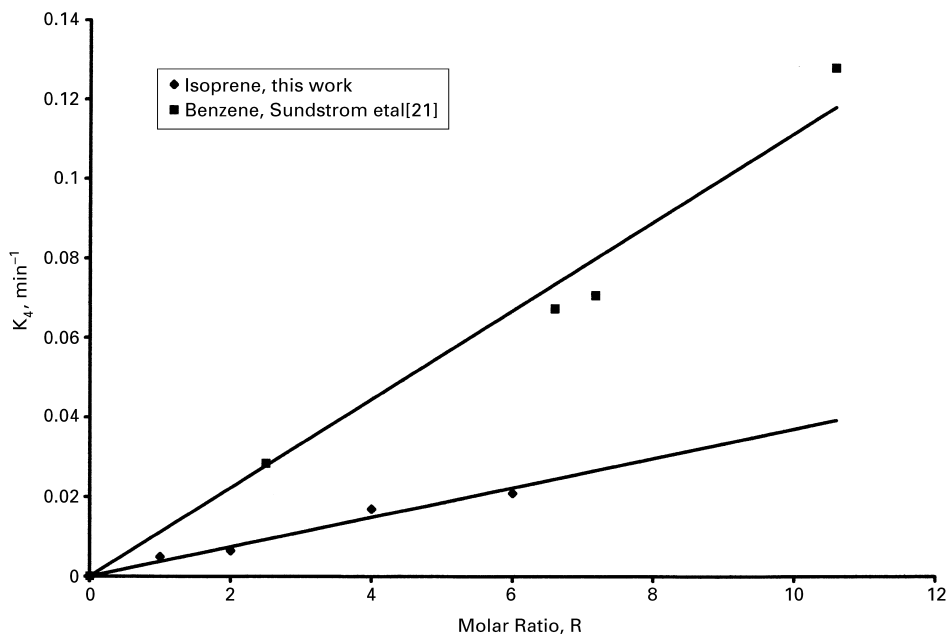
Molar ratio <i>R</i>	$k_3 + k_4$ (min <sup>-1</sup> )	AAD%	STDD	95% CL	$k_4$ (min <sup>-1</sup> )	$(k_3 + k_4)/k_3$
0.0	0.022 ( $k_4 = 0$ )	7.2	0.0019	0.0057	0.0	1.0
1.0	0.027	5.0	0.0018	0.0054	0.005	1.23
2.0	0.0287	6.6	0.0025	0.0075	0.0065	1.3
4.0	0.038	8.6	0.004	0.012	0.017	1.81
6.0	0.042	9.5	0.005	0.015	0.021	2.0

CL = confidence level.

STDD = standard deviation.

AAD% = percent average absolute deviation =  $(1/N)100\sum|X^{\text{exp}} - X^{\text{prd}}|/X^{\text{exp}}$ ;  $N$  = number of data points;  $X^{\text{prd}}$  = value predicted by model;  $X^{\text{exp}}$  = experimental value.

The sum of the apparent rate constants ( $k_3 + k_4$ ) and the reaction order  $n$  were determined from the data of the combined effects of UV alone and UV/H<sub>2</sub>O<sub>2</sub> reactions. The value of  $n$  was found to be 1, as shown in the semi-log plots of isoprene fractional concentration remaining ( $-\ln C_H/C_0$ ) over the times of reaction of Fig. 4. In fact, most of the semi-log plots were linear over the periods of reaction time considered. These results indicate that the rate expression of Eq. (6) can be assumed to be pseudo-first w.r.t the concentration of isoprene. Semi-log plots of the data on UV only also showed first order kinetics w.r.t. to isoprene as shown in Fig. 4. The values of  $k_3$ ,  $k_3 + k_4$  for

Fig. 5. Relation between  $k_4$  and the molar ratio,  $R$ .

various  $\text{H}_2\text{O}_2$ :isoprene ratios and the ratio  $o(k_4 + k_3)/k_3$  are listed in Table 1. Statistical analysis in Table 1, shown for first order fit of the data, are better than those for other reaction orders. A plot of  $k_4$  against the molar ratio of  $\text{H}_2\text{O}_2$  to isoprene shown in Fig. 5 gave a straight line passing through the origin. It can be seen from this plot, and noting that  $\text{H}_2\text{O}_2$  is being consumed during the reaction, that the value of  $k_4$  is proportional to the amount of  $\text{H}_2\text{O}_2$ ; a characteristic of pseudo-catalyzed reactions where the rate of reaction increases linearly with the increase of the amount of catalyst. For comparison with other  $\text{H}_2\text{O}_2$ /UV degradation of VOCs in aqueous solutions, the results of Sundstrom et al. [21] for benzene were also plotted in Fig. 5. A similar trend can be noticed where  $k_4$  varies linearly with  $R$ . These results together with the results of Fig. 3, confirm that  $\text{H}_2\text{O}_2$  acts as a pseudo-catalyst that enhances the photolysis reaction.

To investigate the nature of the reaction products, samples were taken during the reaction of isoprene with molar ratios of 1 and 6 and reaction times of 5 and 120 min, respectively. The GC/MS and GC analysis showed some peaks for reaction time of 5 min and molar ratio of 1. Some of these peaks were identified as isoprene, formaldehyde and methyl vinyl ketone. The most significant result is that all the peaks disappeared as the reaction time was extended to 120 min using a molar ratio of 6.

#### 4. Conclusions

Through a series of experiments, the kinetics of the degradation of isoprene by  $\text{H}_2\text{O}_2$ /UV radiation was measured. The degradation process was modeled as two parallel reactions taking place simultaneously: one due to the direct photolysis by UV alone and the other due to the  $\text{H}_2\text{O}_2$  catalyzed photolysis. Correlation of the experimental data to an empirical rate expression, with two rate constants, was found to be pseudo-first order w.r.t. the concentration of isoprene and the apparent kinetic constants were determined. The rate of reaction of isoprene increased with increase in  $\text{H}_2\text{O}_2$ :isoprene molar ratio in a linear fashion. The concentration of  $\text{H}_2\text{O}_2$  was observed constant during the course of the reactions. These findings suggest that  $\text{H}_2\text{O}_2$  acts as a pseudo-catalyst that enhances the photolysis reaction.

Extending the reaction time to 120 min at a molar ratio of six destroyed isoprene and its intermediate products; possibly to carbon dioxide and water.

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