Reinvestigation of the Acetone Degradation Mechanism in Dilute Aqueous Solution by the UV/H₂O₂ Process

MIHAELA I. STEFAN* AND

JAMES R. BOLTON

Department of Chemistry, The University of Western Ontario, London, Ontario, Canada N6A 5B7

A reinvestigation of the UV/H₂O₂ treatment of acetone has revealed previously undetected intermediates (pyruvic acid, pyruvic aldehyde, and hydroxyacetone). The time profiles of the concentrations of all intermediates have been determined, and a detailed mechanism for the degradation steps accounting for all detected intermediates is proposed. A kinetic model was developed on the basis of the proposed mechanism, and the predicted patterns of the reactants and intermediates are in good agreement with the experimental data. The application of the UV/H₂O₂ process to the degradation of acetone results in the eventual mineralization of all organic compounds, as demonstrated by TOC measurements.

Introduction

Since acetone is found in many contaminated waters, a kinetic and mechanistic study was previously undertaken by the authors on the degradation of acetone and its reaction intermediates by the UV/H_2O_2 process until complete mineralization was achieved (1). Our recent reinvestigation of the acetone/ H_2O_2 system under UV light indicated that, apparently due to an analytical problem, some of the degradation intermediates (pyruvic aldehyde, pyruvic acid, and hydroxyacetone) had been overlooked, and consequently the proposed reaction mechanism was incomplete.

Since the above-mentioned paper has been published, only one other paper has emerged in the literature on the treatment of ketones in contaminated waters, but the process used was UV/O₃ (2); however, it does not offer a detailed mechanism of acetone degradation.

The present work presents a complete reaction scheme for the treatment of acetone by the UV/H_2O_2 process under which any organic compound is eventually mineralized.

Experimental Section

Reagents and Materials. All chemicals (analytical reagent grade) were used without any further purification, as mentioned previously (*1*).

Apparatus. The Rayox reactor and the method for the calculation of the fraction of light absorbed individually by acetone and hydrogen peroxide have been described previously in detail (*1*). The total incident photon flux entering the reactor from the UV–Vis 1 kW medium-pressure Hg lamp was $(2.18 \pm 0.10) \times 10^{-4}$ einstein s⁻¹ within the 200–300 nm



FIGURE 1. Decay of acetone and time profiles of main intermediates. Solid lines represent the computer modeling patterns.

range, as determined by potassium persulfate actinometry (*3*) and the spectral emission of the UV lamp.

Analytical Determinations. The acetone and hydroxyacetone concentrations were determined by gas chromatography using a model 6890 Hewlett Packard gas chromatograph and an HP Carbowax ($30 \text{ m} \times 0.53 \text{ mm}$, 0.25 mmthickness) column. The injector and detector (FID) temperatures were 250 and 260 °C, respectively, and helium was used as the carrier gas. By running a temperature program isothermally at 40 °C for 5 min then to 150 °C (hold for 2 min) at a rate of 20 °C/min, acetone and hydroxyacetone were eluted out of the column at retention times of 1.8 and 9.1 min, respectively.

Organic acids were identified and quantified by ionexchange chromatography (IC) performed with a Dionex DX-100 ion chromatograph (conductivity detector). Different IC conditions were developed, depending on the nature of the acids analyzed. An IonPac AS 14 (4 × 250 mm) ion exchange column preceded by an AG 14 guard column was used for the analysis of acetic, formic, and pyruvic acids with a 3 mM Na₂B₄O₇ solution as the eluent (isocratic flow of 1.45 mL min⁻¹). The same column was employed for the analysis of oxalic acid but with 9 mM Na₂B₄O₇ as the eluent (isocratic flow of 1.65 mL min⁻¹). Since under the above conditions glyoxylic acid coelutes with acetic acid, the IonPac AS 10 (4 × 250 mm) analytical column preceded by the AG 10 guard column with 80 mM NaOH solution as eluent was used for the analysis of the glyoxylic acid concentration.

Aldehydes were quantitatively determined as hydrazones by an HPLC method (4). Formaldehyde was also estimated by Hantzsch reaction (5), and the results agreed very well with the HPLC measurements. Hydrogen peroxide was destroyed with 0.5% catalase aqueous solution (5 μ L/20 mL of sample) in those samples subjected to analysis for organic acids and aldehydes. Hydrogen peroxide and the total organic carbon have been analyzed as mentioned previously (1).

Results and Discussion

Acetone Decay and Degradation Products. When a ~ 1.1 mM acetone and 15 mM H₂O₂ aqueous solution was irradiated, acetic, pyruvic, and oxalic acids and pyruvaldehyde were identified and quantified as major degradation products (Figure 1), whereas formic and glyoxylic acids, hydroxyacetone, and formaldehyde were considered as minor products (Figure 2). A list for the rate constants for the reaction of OH

^{*} Corresponding author e-mail: mstefan@julian.uwo.ca; tel: (519)-663-3178; fax: (519)661-3022.



FIGURE 2. Time profiles of minor intermediates. Solid lines represent the computer modeling patterns.



FIGURE 3. Total organic carbon (TOC) balance.

radicals with the organic compounds present in the investigated system was given in the previous paper (*1*). The missing value therein and known in the literature is that for pyruvate ion { $k = 3.1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ (*6*); p $K_a = 2.93$ (*7*)}.

The TOC balance (Figure 3) confirms that all significant intermediates have been identified, quantified, and eventually degraded.

Reaction Mechanism during the UV/H₂O₂ Treatment of Acetone. As noted in the Introduction, the reaction mechanism proposed in the previous paper (1) did not account for the formation of pyruvic aldehyde, hydroxyacetone, and pyruvic acid. We propose a new mechanism for the generation of the acetone degradation products, as outlined in Schemes 1 and 2 and eqs 1 and 2. The degradation paths toward the complete mineralization of some of byproducts were described previously (1) and will not be repeated in this paper.

Pyruvic aldehyde (5), hydroxyacetone (6), formaldehyde (8), and acetic acid (16) are the primary degradation intermediates as generated from the acetonylperoxyl radical (2). Zegota et al. (8) measured the bimolecular decay rate of the acetonylperoxyl radical as $2k = 8 \times 10^8 \, \text{M}^{-1} \, \text{s}^{-1}$ in pulse radiolysis studies. The formation of a tetroxide (3) is generally accepted in peroxyl radical chemistry (9). It can convert through various pathways, such as disproportionation (Russell mechanism), to pyruvic aldehyde (5) and hydroxyacetone (6); H₂O₂ elimination by an electrocyclic process (10)

SCHEME 1. Degradation Pathways of Acetone to the Primary Intermediates



producing pyruvaldehyde; or fragmentation to the acetonyloxyl radical (**4**). The latter undergoes β -scission to formaldehyde and the acetyl radical (**9**), disproportionation in the solvent cage, or fast isomerization by 1,2-H shift (waterassisted process) to a carbon-centered radical (**7**), which finally leads to pyruvic aldehyde (**5**) through HO₂[•] elimination.

The presence of acetic acid at very early stages of irradiation indicates that it is a primary product. It could be formed by cross-termination reactions, as suggested by Zegota et al. (8) and as shown below:

$$CH_{3}C(O)O_{2}^{\bullet} + {}^{\bullet}O_{2}CH_{2}COCH_{3} \rightarrow CH_{3}COO^{-} + H^{+} + CH_{3}COCHO + O_{2}$$
(1)

$$CH_{3}C(O)O_{2}^{\bullet} + CH_{3}O_{2}^{\bullet} \rightarrow CH_{3}COO^{-} + H^{+} + HCHO + O_{2}$$
(2)

Reaction 1 should prevail over reaction 2 due to the higher concentration of acetonylperoxyl radicals (2) as compared with that of methylperoxyl radicals (11). The latter would lead primarily to formaldehyde (11). Pyruvic aldehyde (5) exists mostly in its hydrated form (12) and is assumed to react very rapidly with 'OH radicals by H-abstraction at the formyl group (Scheme 2), being oxidized to pyruvic acid (14). Similarly, hydroxyacetone (6) should be oxidized to pyruvic acid through pyruvic aldehyde as an intermediate.

Scheme 2 includes the proposed mechanism for the degradation of pyruvic acid, mostly present in its ionized form. Dark experiments conducted on a 0.25 mM pyruvate/5 mM H_2O_2 system indicated a significant conversion of pyruvate to acetate, for which a rate constant of 0.11 M^{-1} s⁻¹ was calculated. The reaction consists of the addition of H_2O_2 to the double bond of the carbonyl group leading to the adduct **15**, which decarboxylates by C–C bond cleavage. Similar behavior has been observed with glyoxylic acid (*1*, *12*, *13*) and could explain the rapid decay of pyruvate as compared to that expected only from the light-induced oxidation.

Reactions with •OH radicals provide other routes of acetic acid (16) generation from pyruvic acid. One of the two



possible attack sites of 'OH radicals, depicted in Scheme 2, is at the methyl group generating the carbon-centered radical **18**. β -Scission of radical **18** leading to ketene (**19**) should prevail over reaction with oxygen (dashed arrow route in Scheme 2), since ketomalonaldehyde (**23**) and ketomalonic acid were not detected among the degradation products. The ketene (**19**) instantly generates acetic acid by hydration. Since acetic acid is rapidly generated from pyruvic acid and builds up in the solution because of its slow oxidation rate by the 'OH radicals, it is hard to distinguish whether the low levels of formaldehyde (maximum 0.02 mM) detected during the irradiation of an aqueous solution of 0.7 mM pyruvate and 8 mM H₂O₂ result from the β -scission of the oxyl radical **21** or from an acetate oxyl radical.

Considering the behavior of ketomalonic acid in aqueous solution (14), pyruvic acid should exist in solution to a certain extent in its hydrated form. Therefore, H-abstraction from the hydrated pyruvate leading to the oxygen-centered radical **17** is also possible, followed by C-C bond cleavage with the generation of the acetate ion (**16**) and carboxyl anion radical.

The reaction schemes for the degradation of the acetic, formic, glyoxylic, and oxalic acids to CO_2 and H_2O are given in previous papers (1, 15) and references therein. However, we should mention that in those reactions the organic acids (except for acetic acid, $pK_a = 4.75$) are mostly in their ionized forms considering the pH values measured during the treatment. In the case of oxalic acid, the monoionized form is preponderant, which reacts with the 'OH radical by electron transfer:

$$HOOCCOO^- + {}^{\bullet}OH \rightarrow H_2O + CO_2 + {}^{\bullet}CO_2^- \qquad (3)$$

The calculated fractions of UV light absorbed by H_2O_2 and the quantified organic compounds at different irradiation times show that H_2O_2 remains the main absorber during the experiment, so that direct photolysis of acetone and of degradation byproducts cannot be expected. Consequently, the oxidation processes are strongly dependent on the rate



constants for the reaction of the 'OH radical with each compound and also on their relative concentrations at a given irradiation time.

Kinetic Model. A kinetic model was developed using the same assumptions as in the earlier paper (1), except that the calculation was performed on an Excel spreadsheet with time intervals of 2 s. A value of $G = 1.88 \times 10^{-4}$ einsteins s⁻¹ and a truncated reaction scheme as shown in Scheme 3 were used. The rate constants were the same as those listed in the earlier paper (1) with the following additions:

 $^{\circ}\text{OH}$ + pyruvaldehyde 7.0 × 10⁸ M⁻¹ s⁻¹ (6)

*OH + pyruvic acid $6.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ (assumed) p $K_a = 2.93$ (7)

 $^{\circ}$ OH + pyruvate 6.0 × 10⁷ M⁻¹ s⁻¹ (assumed)

pyruvic acid + H_2O_2 (dark) 0.11 M⁻¹ s⁻¹ (experimental)

 $^{\circ}$ OH + gyloxylic acid 1.5 × 10⁸ M⁻¹ s⁻¹ (assumed)

 $^{\circ}$ OH + hydroxyacetone 8.0 × 10⁸ M⁻¹ s⁻¹ (assumed)

The model fits in the figures are very satisfactory. The disagreement exhibited in the decay curves for oxalic and glyoxylic acids may be due to the contribution of the intermediates to the total light absorbed in the system by the end of the experiment, which is not accounted by the model. Note that the decays of acetone and H_2O_2 are very well predicted without the assumptions of recycling of acetone and a lower quantum yield (0.8 vs 1.0 used here) for H_2O_2 photolysis as were made in the previous paper (1).

Acknowledgments

This work was supported financially by a Collaborative Research and Development Grant jointly funded by the Natural Science and Engineering Research Council of Canada and Calgon Carbon Corporation, Markham, Ontario, Canada. We are thankful to Dr. Stephen Cater, Dr. Ali Safarzadeh-Amiri, and Mr. Keith Bircher of Calgon Carbon Corporation for their helpful comments and support during this research.

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Received for review August 19, 1998. Revised manuscript received December 15, 1998. Accepted December 21, 1998.

ES9808548