

Microwave photochemistry V: Low-pressure batch and continuous-flow microwave photoreactors with quartz mercury electrodeless discharge lamps. Photohydrolysis of mono-chloroacetic acid

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Abstract

BACKGROUND: Low-pressure batch and continuous-flow microwave photoreactors were equipped with microwave powered quartz mercury electrodeless discharge lamps (Hg-EDLs). Photohydrolysis of aqueous mono-chloroacetic acid (MCAA) into hydroxyacetic acid and HCl was chosen as the model reaction to evaluate these photoreactors. The effects of operational parameters on the MCAA photolysis through a UV/MW process were investigated.

RESULTS: Studies were carried out at relatively high MCAA concentration (0.1 mol L^{-1}). The photoreaction course was monitored by the pH change in the solution. The MCAA conversion was optimized as a result of a trade-off between the thermal dependence of the photochemical quantum yield (which increases with increasing temperature) and the thermal dependence of the EDL light intensity of 254 nm line (which increases with decreasing temperature). The microwave photoreactors made it possible to study the temperature dependence of MCAA photohydrolysis.

CONCLUSION: It was found that operational parameters (i.e. reaction temperature, quantum yield) had important effects on photoefficiency. Photohydrolysis of MCAA in the microwave photoreactors can be enhanced by the UV/MW system. The results of conversions (in 120 min) for the particular photoreactor set-ups show that the best reaction conditions for MCAA photolysis were obtained in the low-pressure batch microwave photoreactor (the conversion was 46% at 80°C).

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Keywords: microwave photochemistry; mercury electrodeless discharge lamp; low-pressure photoreactor; continuous-flow photoreactor; photohydrolysis; mono-chloroacetic acid

INTRODUCTION

The photochemical reactors used for the microwave-assisted experiments are essential tools for the present experimental work.¹ Such equipment allows for simultaneous irradiation of the reaction mixture with both microwave and UV/Vis radiation. The objective of microwave photochemistry is frequently, but not necessarily, connected with the electrodeless discharge lamp (EDL) which generates UV/Vis radiation when placed in the microwave field.^{1,2}

In recent papers and reviews on microwave photochemistry¹ we have described the preparation of EDLs,³ spectral characteristics of the lamps,⁴ and their application in organic photochemical synthesis^{2,5,6} and in the microwave photocatalytic decomposition of mono-chloroacetic acid over nanoporous titania thin film.⁷

Photolysis in microwave batch reactors has previously been described.¹ In these arrangements the EDL was placed in a reaction vessel located in a microwave oven and the reaction mixture was irradiated with UV/Vis radiation and microwaves. The intense infrared output from the EDL triggers immediate boiling of solvents. This equipment provides the possibility for studying photochemical reactions under extreme thermal

conditions.¹ However, technical difficulties occur when the microwave photochemical experiments are to be performed at temperatures below the boiling point of the solvent. Therefore a simple low-pressure operating microwave photoreactor was constructed and applied.

Microwave-assisted photolysis in continuous-flow reactors can be implemented if external or internal lamps (classical UV lamp vs EDL) are used. The combination of variables may lead to the following three types of techniques for continuous-flow set-up in a microwave field:

- classical UV lamp + MW field;^{8,9}
- EDL (reaction mixture without MW field);^{10–14} and
- EDL + MW field.^{15–23}

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The considerable improvement of photolysis in a continuous-flow system using a combination of classical UV light and microwave radiation (type a) was reported for the oxidative decomposition of aqueous phenol in H_2O_2 ,⁸ even if the thermal effect was suppressed. Similarly, an ionizer for oxidation of organic contaminants in water has been described.⁹

Photochemical experiments in a continuous-flow reactor were performed using the EDL^{10–12} as UV/Vis irradiation source, without considering the effects of microwaves on the photoreaction (type b). Holroyd and Bielski¹³ developed a photochemical apparatus for generating superoxide radicals ($\text{O}_2^{\cdot-}$) in an oxygen-saturated aqueous sodium formate solution by means of a vacuum-UV EDL (quartz, Xe, Ar). Also, a novel UV-oxidation system with a simple coaxial flow-through reactor and with a high-efficiency microwave Hg-EDL was used to remove toxins or pathogens from water.¹⁴

Direct photolysis under simultaneous UV/Vis (from EDL) and microwave irradiation (type c) has been developed into many applications. This arrangement provided a unique possibility for studying photochemical reactions under extreme conditions. A flow-through photoreactor for disinfecting drinking, waste, and feed-water has been designed.¹⁵ Also a microwave sterilizer was described.¹⁶ Spherical or cylindrical EDLs¹⁷ have been used to remediate air, water, or other fluids. The microwave-assisted degradation of 4-chlorophenol by direct photolysis^{18,19} was compared with that by TiO_2 photocatalysis in the Hg-EDL system. Synergistic effects of several microwave-assisted advanced oxidation processes (MW/AOPs) were studied for the degradation of 4-chlorophenol (MW/UV/ H_2O_2).²⁰ The photolytic degradation²¹ and oxidative decomposition (in the presence of H_2O_2) of the azo dye Acid Orange 7 was studied.²² Also, a continuous-flow microwave photocatalytic reactor with titania-coated EDLs was designed recently.²³

This paper describes a new approach to the photohydrolysis of mono-chloroacetic acid (MCAA) in batch and continuous-flow microwave photoreactors with Hg-EDLs together with the examination of operating parameters (reaction temperature, quantum yield) influencing the photoreaction course. The MCAA was chosen as a model water pollutant due to the easy potentiometric determination of H^+ ions.²⁴

MATERIALS AND METHODS

Chemicals

Mono-chloroacetic acid (MCAA) (99%) (Lachema, Czech Republic), hydrochloric acid (Lachema, CR), glycolic acid (HAA) (99%) (Aldrich, Germany), and mercury (99.9999%) (Aldrich) were used as obtained. All solutions were prepared using distilled water (conductivity $1\ \mu\text{S cm}^{-1}$). The fused quartz tube equipment (Ilmasil® PN) was produced by QSIL AG Quarzschmelze Ilmenau (Langwiesen, Germany). Argon (5.0 grade) was purchased from Linde Technoplyn (Prague, CR).

Preparation of EDLs and spectral measurements

The vacuum system pattern for the preparation of the quartz mercury EDLs has been described previously (2.5 μL Hg, 20 Torr Ar, 6 cm of stainless steel thin wire as a spiral).³ The lamp length was 50 mm (diameter 20 mm).

Spectral measurements of the prepared quartz Hg-EDLs (light intensity for 254 nm line of Hg) were carried out using a USB2000 spectrometer with optic fiber probe (P300-2-SR, solarization-resistant assemblies, 200–1100 nm) and operating software package Oolirrad-C (Ocean Optics, Dunedin, FL, USA).^{3,4}



Figure 1. Low-pressure batch microwave photoreactor.

Photochemical batch experiments

Aqueous MCAA (250 mL; $0.1\ \text{mol L}^{-1}$) was irradiated in a classical immersion-well photoreactor (300 mL) containing a medium-pressure UV lamp (RVK 125, Teslamp, Prague, CR) in a water-cooled double jacket (quartz glass).⁵

Microwave experiments in the batch set-up were accomplished in a microwave oven (Panasonic NN-GD566 with inverter, 1000 W; or MicroSYNTH Labstation, 1000 W, Milestone, Italy) described elsewhere.^{3,5} The aqueous MCAA (250 mL; $0.1\ \text{mol L}^{-1}$) (500 mL round-bottom flask equipped with a magnetic stirrer, a fiber-optic temperature probe, and a Dimroth condenser) was irradiated by the quartz Hg-EDL placed into the reaction solution. Temperature of the mixture was maintained at reflux ($100\ ^\circ\text{C}$).

The set-up for the low-pressure batch microwave photoreactor included (in addition to the batch equipment) the vacuum system LABOPORT SC 810.3 (membrane pump, base plate, condenser, separator, and one vacuum controller; KNF Neuberger GmbH, Freiburg, Germany). The lower reaction temperature during MCAA photolysis in a microwave field was achieved by altering the total pressure of the system by pump (Fig. 1). The measured values of temperature (T in $^\circ\text{C}$) at a given total pressure (p in mbar) were fitted to an exponential growth curve ($R = 0.9999$) and the obtained dependence was used to adjust the required reaction temperature, i.e. $40\ ^\circ\text{C}$ (61 mbar), $50\ ^\circ\text{C}$ (114 mbar), $60\ ^\circ\text{C}$ (190 mbar), $70\ ^\circ\text{C}$ (298 mbar), $80\ ^\circ\text{C}$ (454 mbar), and $90\ ^\circ\text{C}$ (677 mbar).

Microwave photochemical experiments in the continuous-flow set-up

The experimental set-up for the continuous-flow microwave photoreactor is depicted in Fig. 2.²³ The aqueous mixture of MCAA (total fluid volume 500 mL; $0.1\ \text{mol L}^{-1}$) was circulated

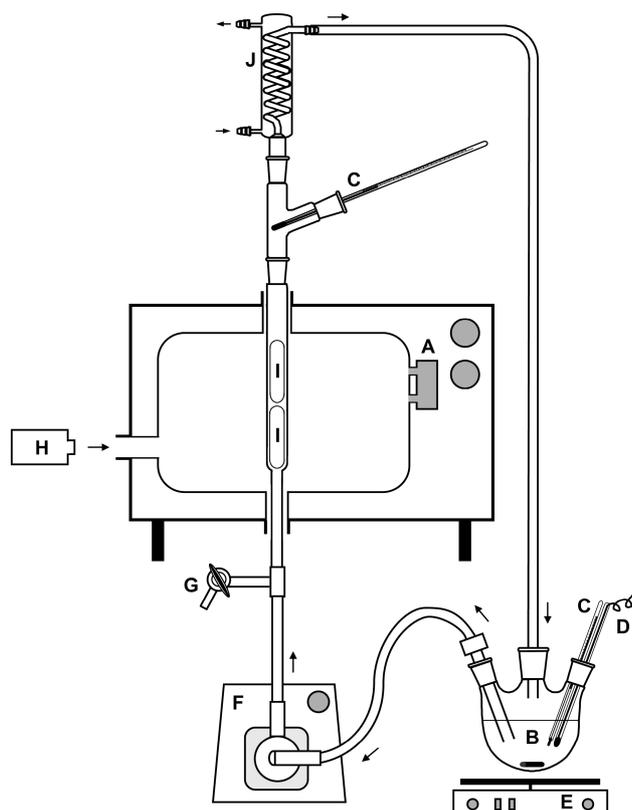


Figure 2. Schematic diagram of the continuous-flow microwave photoreactor. (A) modified microwave oven with magnetron; (B) glass reservoir with magnetic stir bar; (C) thermometer; (D) pH-meter with a glass electrode; (E) magnetic stirrer; (F) PTFE diaphragm pump; (G) outlet; (H) spectrometer with a fiber-optic probe; (I) quartz tube with the quartz Hg-EDLs; and (J) cooling condenser.

through the photoreactor system consisting of the glass reservoir (B) (500 mL; fitted with a thermometer (C) and a pH meter with glass electrode (D)) connected by tubing (ISO Versinic, Saint-Gobain, France) to a PTFE diaphragm pump (F) (Cole-Parmer, Masterflex, Vernon Hills, IL, USA), a quartz tube (200 mm (length) \times 22 mm (internal diameter)) with the quartz mercury EDLs (I) inside a modified microwave oven (A), and a cooling condenser (J). When the constant microwave power (900 W) was switched on, the quartz Hg-EDLs (I) started to emit UV/Vis radiation. The desired temperature in the continuous-flow photoreactor was achieved by adjustment of the pump flow rate.

Analysis

The pH of the aqueous solution was monitored every 20 min using a combined glass electrode (D) (Fig. 2) connected to a digital pH/mV meter (Inolab Level 1, WTW, Weilheim, Germany). The pH of each solution was measured immediately after calibration (standard buffer solutions of pH 4.0, 7.0 and 10.0 obtained from WTW) of the electrode system. The results of pH measurements showed good reproducibility (RSD = 2.07%, $n = 10$).

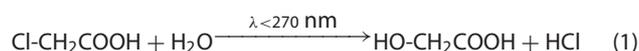
The stock solutions of acids were prepared by accurate weighing of MCAA, HAA, HCl followed by dissolution in distilled water. Standard solutions of the aqueous acid mixtures at various concentrations (c_{MCAA} , c_{HAA} and c_{HCl}) were prepared by mixing the respective stock solutions according to the required values (0.100 to 0.001 mol L⁻¹). The pH of standard solutions was measured by the pH meter.

Results of the pH measurements were compared with those obtained by NMR spectroscopy. ¹H and ¹³C NMR spectra were recorded on a Varian Mercury VX300 instrument using *t*-butyl alcohol (δ 1.23; 29.74) as internal standard; Cl-CH₂CO₂H (MCAA): δ 4.17 (s, 2H, CH₂) [lit.²⁵], 41.34 (s, 1C, CH₂) and 171.99 (s, 1C, CO₂H) [lit.²⁶]; HO-CH₂CO₂H (HAA): δ 4.23 (s, 2H, CH₂) [lit.²⁷], 59.42 (s, 1C, CH₂) and 176.04 (s, 1C, CO₂H) [lit.²⁷]. Chemical shifts are quoted in ppm (s, singlet), solvent D₂O.

No other intermediates from MCAA degradation (such as acetic acid, formaldehyde) were observed under these concentration and thermal reaction conditions.²⁸

RESULTS AND DISCUSSION

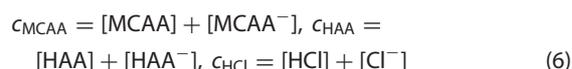
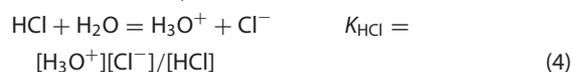
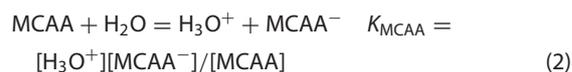
The mono-chloroacetic acid (MCAA) photohydrolysis to hydroxyacetic acid (HAA) and hydrochloric acid has been investigated in chemical actinometry^{28–30} and can be written as follows:



MCAA absorbs UV radiation at $\lambda < 270 \text{ nm}$ ^{28–30} and the intensity of the absorption band ($\epsilon_{254} = 2.5 \text{ L mol}^{-1} \text{ cm}^{-1}$) suggests the $n\pi^*$ transition. The most probable primary photoreactions are the homolytic C–Cl bond cleavage and the hydrolysis of excited singlet states.²⁸ The formation of the $\cdot\text{CH}_2\text{COOH}$ radical as a primary photolytic product was verified by ESR techniques.²⁸

The pH calculation and measurement of the water–acid mixtures

The pH of the aqueous acid mixtures can be described in the general approach for the solution equilibrium by a set of equations as follows:



where Equations (2)–(4) are the protolytic equilibria characterized by the concentration dissociation constants K^C , Equation (5) is a charge balance, i.e. the solution must be neutral (electroneutrality condition), and Equations (6) are mass balances that reflect that the sum of concentrations of all acid forms present in the solution and must be identical to the concentration of acid added or originated. After editing and certain simplification ($c_{\text{MCAA}} = 0.1 - c_{\text{HAA}} = 0.1 - c_{\text{HCl}} = 0.1 - c$; $K_{\text{HCl}} \approx K_{\text{HCl}} + [\text{H}_3\text{O}^+]$; the last term $K_w/[\text{H}_3\text{O}^+]$ can be neglected) we get the following equation:

$$[\text{H}_3\text{O}^+] = \frac{K_{\text{MCAA}}(0.1 - c)}{K_{\text{MCAA}} + [\text{H}_3\text{O}^+]} + \frac{K_{\text{HAA}}}{K_{\text{HAA}} + [\text{H}_3\text{O}^+]} + c \quad (7)$$

which when expanded gives the cubic equation that can be solved (after calc. of K^C) for the molar concentration of hydroxonium ions ($[\text{H}_3\text{O}^+]$) with Cubic equation solver³¹ (*vide infra*).

Table 1. Quantified values of the individual acid concentrations (c_{MCAA} , c_{HAA} and c_{HCl}), the degree of dissociation (α_{MCAA} , α_{HAA}), the ionic strength of the solution (I), the concentration dissociation constants (K_{MCAA} and K_{HAA}), the molar concentration of hydroxonium ions ($[H_3O^+]$), the mean activity coefficients (γ_{\pm}), and the pH of water–acid solutions

c_{MCAA} (mol L ⁻¹)	c_{HAA}, c_{HCl} (mol L ⁻¹)	α_{MCAA}	α_{HAA}	I (mol L ⁻¹)	$K_{MCAA} \times 10^3$	$K_{HAA} \times 10^4$	$[H_3O^+]$ (mol L ⁻¹)	γ_{\pm}	pH
0.100	0	0.1108	–	0.011	1.71	–	0.012	0.898	1.97
0.099	0.001	0.1113	0.3178	0.012	1.72	1.85	0.013	0.893	1.94
0.095	0.005	0.1135	0.1579	0.017	1.77	1.90	0.015	0.880	1.88
0.090	0.010	0.1164	0.1145	0.022	1.83	1.96	0.018	0.867	1.81
0.085	0.015	0.1196	0.0945	0.027	1.87	2.01	0.022	0.856	1.72
0.080	0.020	0.1230	0.0824	0.031	1.91	2.05	0.026	0.847	1.66
0.070	0.030	0.1309	0.0678	0.041	1.98	2.12	0.034	0.833	1.55
0.060	0.040	0.1406	0.0590	0.051	2.04	2.18	0.043	0.821	1.45
0.050	0.050	0.1529	0.0529	0.060	2.09	2.23	0.052	0.811	1.38
0.040	0.060	0.1693	0.0484	0.070	2.13	2.28	0.062	0.802	1.30
0.030	0.070	0.1927	0.0449	0.079	2.17	2.32	0.071	0.795	1.25
0.020	0.080	0.2304	0.0421	0.088	2.20	2.36	0.081	0.789	1.19
0.010	0.090	0.3088	0.0397	0.097	2.23	2.39	0.090	0.784	1.15
0	0.100	–	0.0377	0.104	–	2.41	0.100	0.780	1.11

The semi-empirical Debye–Hückel relationship proposed by Davies³² at 25 °C and for the relative low solute concentrations ($I < 0.5 \text{ mol L}^{-1}$) was used to calculate the concentration dissociation constant (K^C) from the thermodynamic dissociation constant (K^T) as follows:

$$pK^C = pK^T - \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right) \quad (8)$$

where $K_{MCAA}^T = 0.00138$ [lit.³³], $K_{HAA}^T = 0.000148$ [lit.³⁴], and I is the solution ionic strength. The I was calculated for the individual acid concentrations (c_{MCAA} , c_{HAA} and c_{HCl}) according to Equation (9) after the value substitution as follows:

$$I = c_{MCAA}\alpha_{MCAA} + c_{HAA}\alpha_{HAA} + c_{HCl} \quad (9)$$

where α is the degree of dissociation (it was calculated from the well-known quadratic equation, $K^C(1 - \alpha) = c\alpha^2$).³⁵ The quantified values of the concentration dissociation constants (K_{MCAA} and K_{HAA}) and the ionic strength (I) for the acid concentrations are reported in Table 1.

The pH values measured by potentiometry with a glass electrode indicate the activity of hydroxonium ions ($a_{H_3O^+}$). The pH for water–acid mixtures can be calculated from the molar concentration of hydroxonium ions ($[H_3O^+]$, Equation (7)) as follows:

$$pH = -\log a_{H_3O^+} = -\log \gamma_{\pm}[H_3O^+] \quad (10)$$

where γ_{\pm} is the mean activity coefficient of ions given in the Davies equation (applicable for aqueous solutions at 25 °C and $I < 0.5 \text{ mol L}^{-1}$)³² as follows:

$$\log \gamma_{\pm} = -0.509 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right) \quad (11)$$

where I is the solution ionic strength calculated from Equation (9).

The final calculation of pH for acid mixtures can be obtained through Equation (10) by using the values of the mean activity

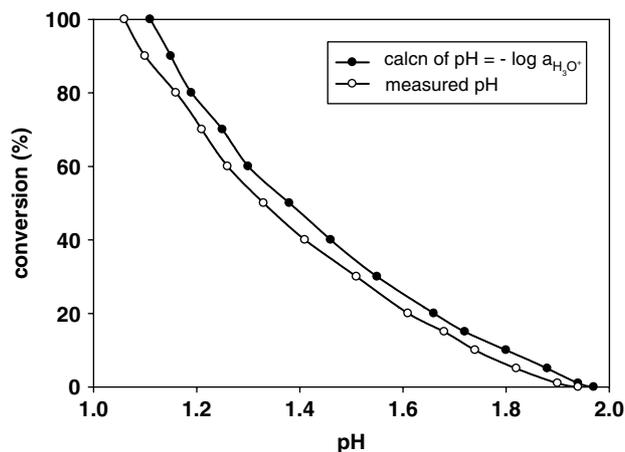


Figure 3. MCAA photo-conversion as a function of the pH values.

coefficient (γ_{\pm}) (Equation (11)) and the molar concentration of hydroxonium ions ($[H_3O^+]$) (Equation (7)) reported in Table 1.

The MCAA photo-conversion as a function of the pH values is illustrated by the graph in Fig. 3. The calculated pH values (solid circles) were compared with the measured pH values (open circles) of prepared calibration acid solutions (see the experimental part). The measured pH values at given conversions were fitted with an exponential decay curve ($R = 0.9999$). The dependence obtained was used for the MCAA photo-conversion calculation from the experimentally measured pH values.

Temperature effect on photohydrolysis of mono-chloroacetic acid

MCAA photohydrolysis was studied first in a classical immersion-well photoreactor equipped with a medium-pressure UV lamp (RVK 125). MCAA solution (0.1 mol L^{-1}) was irradiated at room temperature and the time dependence of MCAA conversion is shown in Fig. 4 (open circles). The results demonstrate that MCAA conversion in 120 min was only 4%.

The microwave photo-experiments in the batch set-up were carried out in a round-bottom flask equipped with a quartz

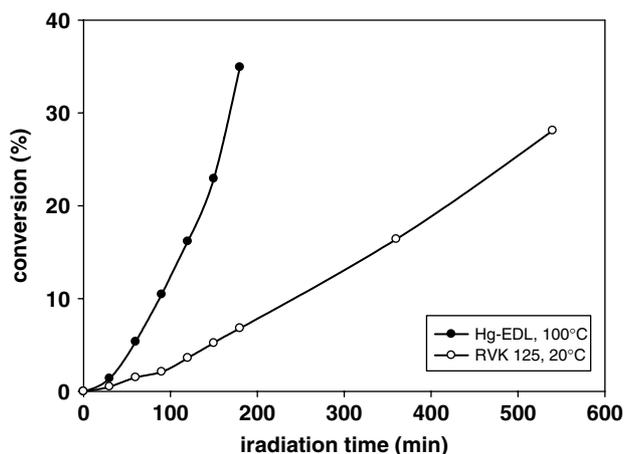


Figure 4. Time dependence of MCAA conversion with UV lamp type (RVK 125, quartz Hg-EDL) in the batch set-up.

Hg-EDL.^{3,5} Temperature of the photoreaction mixture increased rapidly and was maintained at reflux (about 100 °C). The time dependence of MCAA conversion is shown in Fig. 4 (solid circles). The results revealed that MCAA conversion in 120 min was about 17%. The elevated rate of MCAA photohydrolysis is affected by temperature (100 °C) and by the EDL intensity,¹ which were both higher than in the classical photoreactor with the RVK 125 lamp.

The temperature of the MCAA aqueous medium affects the EDL quartz envelope temperature and therefore the plasma lighting properties.¹ The effect of temperature on the EDL envelope is closely associated with the fill gas pressure and has already been investigated.^{4,36} It was found that the optimum operating temperature for the mercury fill is between 45 and 50 °C (for 254 nm line, $6^1S_0-6^3P_1$).³⁷ The output is strongly reduced when the temperature is beyond optimum. Photochemical operation at high temperatures can decrease the 254 nm line intensity of the EDL. Therefore, the temperature effect on the EDL light intensity at 254 nm was measured (Fig. 5, solid circles). The intensity was appreciably suppressed with increasing temperature from 36 to 98 °C, however, a marked decline near 60 °C was also observed. This rapid output decrease at 60 °C was caused by the 254 nm line sensitivity to self-absorption (distortion of shape and line broadening), which is stronger at higher temperatures.^{38,39} Also, at this temperature a strong reduction in the intensity of the inert gas lines has been observed.³⁶

On the other hand, the rate of MCAA photohydrolysis is also determined and quantified by the quantum yield, defined as $\Phi = (\text{yield of photoproducts})/(\text{number of photons absorbed})$. The variation in the quantum yield of MCAA photohydrolysis with temperature⁴⁰ is shown in Fig. 5 (open circles), and Φ proportionally increases from $\Phi_{\text{MCAA}}(25^\circ\text{C}) = 0.31$ to $\Phi_{\text{MCAA}}(69^\circ\text{C}) = 0.69$ with temperature coefficient $+0.009^\circ\text{C}^{-1}$.³⁰ The temperature effect on the quantum yield is opposite to that on the EDL light intensity of the 254 nm line: therefore the optimal temperature for the photochemical reaction course is about 50 °C (*vide infra*).

Investigations of the temperature effect on the MCAA reaction conversion were also carried out in the low-pressure batch microwave photoreactor (Fig. 1). The temperature of aqueous solution, in the case of microwave photo-experiments in the batch set-up, is usually assigned to the boiling point of water (100 °C). The changes of reaction temperature during MCAA photolysis in

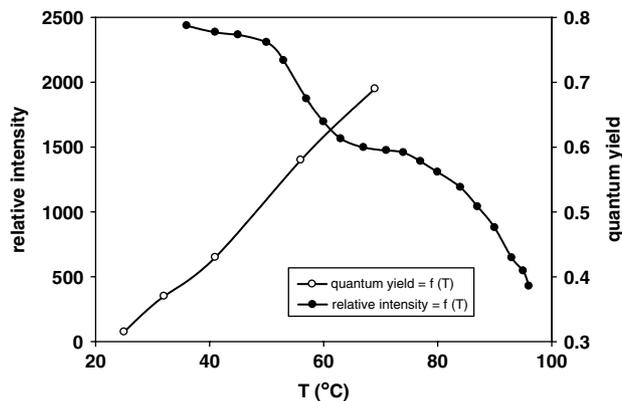


Figure 5. Effect of reaction temperature on the EDL light intensity (of the 254 nm line) and on the quantum yield of MCAA photohydrolysis.⁴⁰

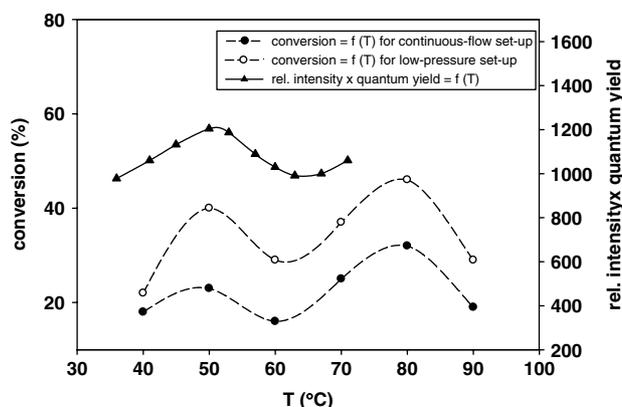


Figure 6. Effect of reaction temperature on MCAA conversion in 120 min and on the product (relative intensity \times quantum yield).

a microwave field can be achieved by altering the total pressure of the system using a pump. The values of temperature at given values of total pressure were used to adjust the required reaction temperature, i.e. 40 °C (61 mbar), 50 °C (114 mbar), 60 °C (190 mbar), 70 °C (298 mbar), 80 °C (454 mbar), and 90 °C (677 mbar). The time dependence of the MCAA conversion in the low-pressure set-up is shown in Fig. 6 (open circles). The results proved that MCAA conversion in 120 min is strongly dependent on reaction temperature, with two maxima (40% at 50 °C and 46% at 80 °C) and several minima (22% at 40 °C, 29% at 60 °C, and 29% at 90 °C). These outcomes are related to the temperature dependence of the 254 nm line of the EDL (Fig. 5, *vide supra*). The local decrease in conversion at 60 °C is an effect of a trade-off between the thermal dependence of the photochemical quantum yield (which increases with increasing temperature; Fig. 5, open circles) and the thermal dependence of the EDL light intensity of the 254 nm line (which increases with decreasing temperature; Fig. 5, solid circles). The product of relative intensity and quantum yield (i.e. $I \times \Phi$) is also plotted in Fig. 6 (solid triangles). This dependence shows again the local minimum at temperature 60 °C, which is in accord with proposals above.

Temperature dependences of MCAA photohydrolysis were also studied in the continuous-flow set-up. The MCAA aqueous solution (0.1 mol L⁻¹) was circulated through the photoreactor system (Fig. 2) that consisted of quartz Hg-EDLs inside a microwave oven. The methodology involving the influence of reaction temperature

on photohydrolysis was carried out within the range from 40 to 90 °C when the reaction temperature was altered by changing the feed flow rate.²³ The MCAA conversion in the continuous-flow set-up was again maximum at 50 °C (23%) and 80 °C (32%) (Fig. 6, solid circles) as a result of the trade-off between the thermal dependence of the photochemical quantum yield and the thermal dependence of the EDL light intensity of 254 nm line (see Fig. 5). The lower MCAA conversions at 40 (18%), 60 (16%) and 90 °C (19%) (Fig. 6, solid circles) were the result of the dominant influence either of the lower quantum yield (at 40 °C) or the lower EDL light intensity (at 90 °C) at the given temperatures. The reason for the local minimum at 60 °C is the same as that mentioned above.

Photoreactor efficiency effect

Comparison of the respective photoreactors is difficult owing to differing reaction conditions (i.e. temperature, UV/Vis source, irradiated amount). However, the results of conversions (in 120 min) allow comparison of the particular photoreactor set-ups and their efficiency:

- 4% (at 20 °C, RVK 125 lamp, 250 mL) in the classical immersion-well photoreactor;
- 17% (at 100 °C, Hg-EDL, 250 mL) in the batch microwave photoreactor;
- 46% (at 80 °C, Hg-EDL, 250 mL) in the low-pressure batch microwave photoreactor;
- 32% (at 80 °C, two Hg-EDLs, 25 mL) in the continuous-flow microwave photoreactor.

In the case of item (a) low conversion (4%) of MCAA photohydrolysis is caused by the lower quantum yield at temperature 20 °C (according to Fig. 5) and the lower relative intensity of 254 nm line in the RVL 125 UV lamp (compared with Hg-EDL).

Conversion (17%) in the batch microwave photoreactor (item (b)) with Hg-EDL is affected by the lower relative intensity (≈ 250 a.u.) at 100 °C (according to Fig. 5) as against the intensity (≈ 1300 a.u.) at 80 °C in the low-pressure set-up (item (c)), where the conversion (46%) was the best. The opposite effect will be expected for the quantum yield at 80 and 100 °C (according to Fig. 5), however, we are assuming the inexpressive increase of values.

Conversion (32%) in continuous-flow set-up (item (d)) is influenced by the different irradiated amount in a quartz tube (25 mL) and the EDL number. Therefore, for practical purposes it would be necessary to use more EDLs.

CONCLUSION

The calculated pH values in the aqueous MCAA photohydrolysis are comparable with the measured pH values. MCAA photolysis into HAA and HCl in the microwave photoreactor was enhanced by the UV/MW system. It was found that the operational parameters (i.e. reaction temperature, quantum yield) considered have important effects on photoefficiency.

The MCAA conversion was optimized through trade-off between the thermal dependence of photochemical quantum yield (which increases with increasing temperature) and the thermal dependence of the EDL light intensity of the 254 nm line (which increases with decreasing temperature).

The results of conversions (in 120 min) for the particular photoreactor set-ups show that the best reaction conditions

for MCAA photolysis were obtained in the low-pressure batch microwave photoreactor (conversion 46% at 80 °C).

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