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The dependence on temperature of gas-phase photocatalytic oxidation of methyl *tert*-butyl ether and *tert*-butyl alcohol

Sergei Preis [a,*], Anna Kachina [a], Nuria Capdet Santiago [b], Juha Kallas [a]

[a] *Department of Chemical Technology, Lappeenranta University of Technology, P.O. Box 20, Lappeenranta 53851, Finland*
[b] *Department of Chemical Engineering, University of Barcelona, c/Martí i Franquès 1-11, Barcelona 08028, Spain*

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Abstract

The influence of temperature on the mechanism and kinetics of gas-phase photocatalytic oxidation (PCO) and thermal oxidation (TO) of methyl *tert*-butyl ether (MTBE) and *tert*-butyl alcohol (TBA) over TiO_2 was studied in a continuous flow annular reactor. The reaction products of PCO of both substances included acetone, water, carbon dioxide and carbon monoxide. Volatile TO products of MTBE included 2-methyl-1-propene (2-MP), carbon monoxide, carbon dioxide and water; TBA decomposed to 2-MP and water. Thermal oxidation of MTBE became noticeable at 388 K, TBA started to decompose thermally at 393 K. Both PCO and TO fit well to the Langmuir–Hinshelwood (L–H) model for monomolecular reactions. The dependence of the kinetic constants on temperature was established in the form of an Arrhenius equation. The TiO_2 catalyst showed no deactivation at temperatures above 373 K but gradually lost its activity below 373 K.

Keywords: Photocatalytic oxidation; Thermal oxidation; Methyl *tert*-butyl ether; *tert*-Butyl alcohol; Titanium dioxide

1. Introduction

Methyl *tert*-butyl ether (MTBE) was the most widely used motor fuel additive in the USA until 1998 and is still the basic oxygenated additive used nowadays in the rest of the world. As a result of massive production of MTBE significant amounts are found in groundwater because of storage tank and pipeline leaks and fuel spills [1]. *tert*-Butyl alcohol (TBA) has been reported as a primary product of photocatalytic degradation and hydrolysis of MTBE in aqueous media [2,3]. Photocatalytic oxidation (PCO) in the aqueous phase is a viable process for elimination of MTBE [2,4], but the slow rate of PCO in the aqueous phase makes gas-phase PCO studies more promising. Air stripping is a reliable technology to remove volatile organic compounds (VOCs) from groundwater, but needs additional pervaporation equipment for MTBE [5]. The MTBE-laden air has to be treated before release to the atmosphere. A few studies have reported PCO of vapour-phase MTBE [6–8], although little information is available on the PCO kinetics and its dependence on temperature.

In the present research, MTBE and TBA oxidation on a TiO_2 surface was studied in its photocatalytic mode with UV-radiation, as was thermal decomposition in the dark within a temperature range of 333–453 K.

2. Experimental methods

The gas-phase PCO of MTBE and TBA over UV-illuminated TiO_2 was studied using an annular photocatalytic reactor in continuous gas-flow mode, having an inner diameter 32 mm, total volume 0.105 L, annular gap (between the lamp and inner wall of the reactor) 3.5 mm, outer diameter of the lamp 25 mm. A 365 nm 15 W low-pressure mercury luminescent UV-lamp was positioned coaxially in the reactor. The reactor assembled with the lamp was coated inside with TiO_2 (Degussa P25) by a 50-times rinse with a TiO_2 aqueous suspension, each rinse followed by drying. Approximately, 0.89 g of TiO_2 coated about 640 cm^2 of the reactor (1.4 mg cm^{-2}). The irradiance of the

* Corresponding author. Fax: +358 5 621 2199.
E-mail address: sergei.preis@lut.fi (S. Preis).

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TiO_2-coated UV-lamp was measured with a UVX Radiometer at the surface next to the lamp and averaged about 0.6 mW cm^{-2} in a 365-nm range.

An evacuated gas cylinder was filled through an injection port with the desired amount of VOC, and then filled with synthetic air (20% O_2, 80% N_2). The VOC-containing stream was blended with a diluent gas to deliver the desired VOC concentration to the reactor. The temperature in the reactor was varied from 333 to 453 K at a gas flow rate 3.5 L min^{-1}, which made the contact time equal to 1.8 s. This detention time was sufficient to reliably register the difference between VOC concentrations in the inlet and outlet streams, keeping that difference within a few ppmv limits to avoid complications caused by intermediate by-products. The temperature was adjusted with heating tape wrapped around the reactor. The tape was controlled with a temperature regulator (Omega CN9000A with a K-type thermocouple). For an airflow rate up to 3.5 L min^{-1}, the lamp heated the insulated reactor to 373 K. Lower temperatures were obtained by removing insulation. The reaction products were analyzed by a Perkin Elmer 2000 FT-IR spectrometer with Sirocco 10.6 m gas cell. Since the volume of the cell was 3.6 L, the time of sampling was 10–15 min for proper averaging. Outlet stream samples were taken three to six times during the 150 min run. Thermal oxidation (TO) of MTBE and TBA was conducted in the same reactor, without UV-radiation, at temperatures from 373 to 453 K. Inlet concentrations of VOC pollutants varied from 20 to 300 ppmv (9×10^{-4} to 1.33×10^{-2} mol L^{-1}). No humidity was introduced to the air stream.

3. Results and discussion

3.1. PCO and TO products

All the reacted TBA and MTBE were stoichiometrically converted to acetone (Eqs. (1) and (2)) [9]; the additional carbon in TBA and MTBE molecules was oxidized to CO_2 (Eq. (3)) along the reactions:

$$\underset{\text{TBA}}{(CH_3)_3C{-}OH} \overset{h^+,O_2}{\Rightarrow} \underset{\text{Acetone}}{(CH_3)_2C{=}O} + H_2O + CH_3\cdot \quad (1)$$

$$\underset{\text{MTBE}}{(CH_3)_3C{-}O{-}CH_3} \overset{h^+,O_2}{\Rightarrow} \underset{\text{Acetone}}{(CH_3)_2C{=}O} + 2CH_3^{\bullet} \quad (2)$$

$$CH_3^{\bullet} \overset{h^+,O_2}{\Rightarrow} \underset{\text{Formic acid}}{HCOOH} \overset{h^+,O_2}{\Rightarrow} CO_2 + H_2O \quad (3)$$

Partial oxidation of acetone resulted in formation of CO [9].

The products of TO of MTBE included 2-methyl-1-propene (2-MP) in a stoichiometric one-to-one ratio with the decomposed MTBE (Eq. (4)). The metoxy-group in the MTBE molecule was thermally oxidised to carbon dioxide and monoxide through the stages of formation of methanol and subsequently formic acid, observed in transient studies elsewhere (Eq. (5)) [9]. TBA decomposed to 2-MP and water with no trace of any other carbonaceous products (Eq. (6)):

$$\underset{\text{MTBE}}{(CH_3)_3C{-}O{-}CH_3} \overset{\text{Heat}}{\Rightarrow} \underset{\text{2-MP}}{(CH_3)_2C{=}CH_2} + CH_3OH \quad (4)$$

$$CH_3OH \overset{\text{Heat},O_2}{\Rightarrow} \underset{\text{Formic acid}}{HCCOH} \overset{\text{Heat},O_2}{\Rightarrow} CO + CO_2 + H_2O \quad (5)$$

$$\underset{\text{TBA}}{(CH_3)_3C{-}OH} \overset{\text{Heat}}{\Rightarrow} \underset{\text{2-MP}}{(CH_3)_2C{=}CH_2} + H_2O \quad (6)$$

3.2. PCO and TO kinetics

Fig. 1 shows the conversions of MTBE and TBA as a result of PCO versus inlet reactant concentrations and temperatures. The conversion varies inversely with the inlet reactant concentration at all temperatures. This kinetic behaviour indicates that the surface reactions are unlikely to be elementary ones: a diffusion-controlled reaction or elementary first order reaction would exhibit constant conversions versus inlet concentration [10].

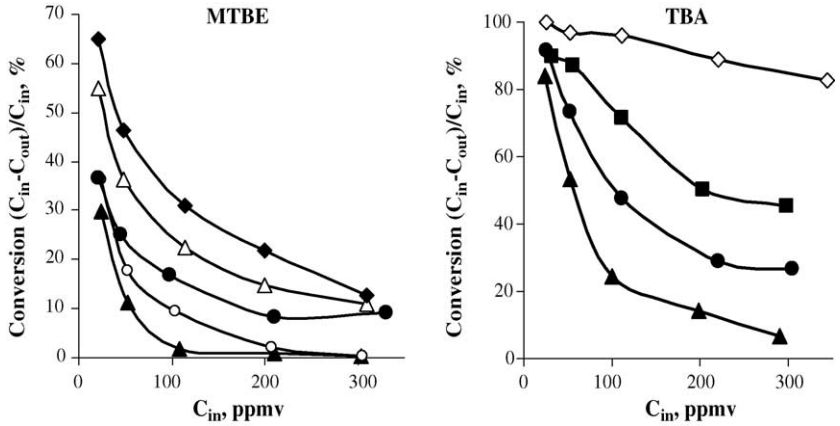

Fig. 1. PCO/TO conversions of MTBE and TBA vs. their inlet concentrations at different temperatures: (▲) 333 K, (○) 353 K, (●) 373 K, (△) 388 K, (◆) 403 K, (■) 413 K, (◇) 453 K.

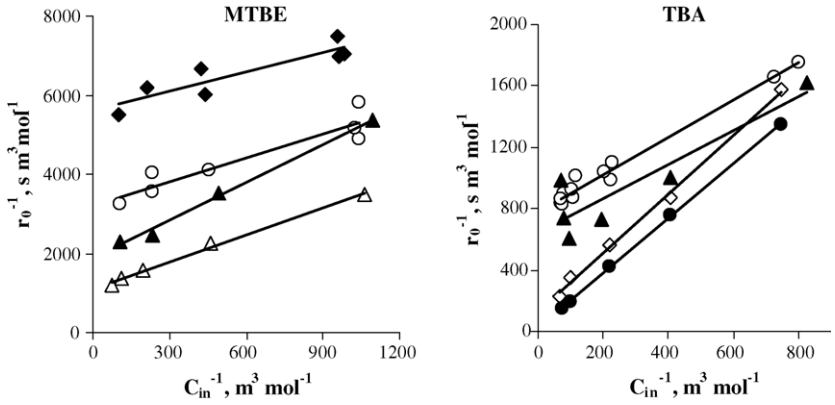

Fig. 2. Reciprocal PCO reaction rates on TiO_2 vs. the reciprocal MTBE and TBA inlet concentrations at: (◆) 333 K, (○) 353 K, (▲) 373 K, (△) 388 K, (◇) 413 K, (●) 453 K.

The Langmuir–Hinshelwood (L–H) model of reaction kinetics has been widely used for gas-phase photocatalytic reactions [8,11,12]. The equation for the simplest monomolecular reaction can be presented as follows:

$$r = \frac{kKC}{1 + KC}, \tag{7}$$

where r is the reaction rate (mol m^{-3} s^{-1}), C is the concentration of reactant (mol m^{-3}), k is the reaction rate constant (mol m^{-3} s^{-1}), and K is the Langmuir adsorption coefficient (m^3 mol^{-1}).

The complex mechanism of photocatalytic reactions with the formation of reaction products makes it difficult to describe the dependence of the photocatalytic degradation rate on the experimental conditions for an extended reaction time in a simple model [12]. Therefore, kinetic modelling of the PCO process is usually restricted to the analysis of the initial rate of photocatalytic degradation. This can be obtained from a minimum detectable conversion of the reactant at a minimum contact time. In our study the initial PCO rate (r_0) of MTBE and TBA was observed to be consistent with the aforementioned L–H kinetic model of the monomolecular reaction. A linear plot of r_0^{-1} versus the VOC's inlet concentration C_{in}^{-1} (Eq. (8)), proving the suitability of the L–H model, is shown in Fig. 2 plotted for the PCO/TO reactions. Values of k and K were obtained:

$$\frac{1}{r_0} = \frac{1}{kK}\frac{1}{C_{in}} + \frac{1}{k} \tag{8}$$

Thermal oxidation contributed to the VOC's decomposition at higher temperatures. An analytically determined difference between the inlet and outlet concentrations of MTBE at 1.8 s contact time was noticed at 388 K. *tert*-Butyl alcohol appeared to be a little more resistant: its thermal decomposition with the noticeable rate started at 393 K. Thermal oxidation reactions in the dark of both VOCs followed the pattern of the conversion degree dependence on the VOC's inlet concentration similar to PCO and thus fitted well the monomolecular L–H kinetics Fig. 3.

The dependence of both PCO/TO and TO apparent rate constants kK on temperature is shown in Fig. 4. One can see that both substances exhibited peculiar behaviour: from 333 to 388 K for MTBE and from 333 to 393 K for TBA the apparent reaction rate constant kK steadily decreased with

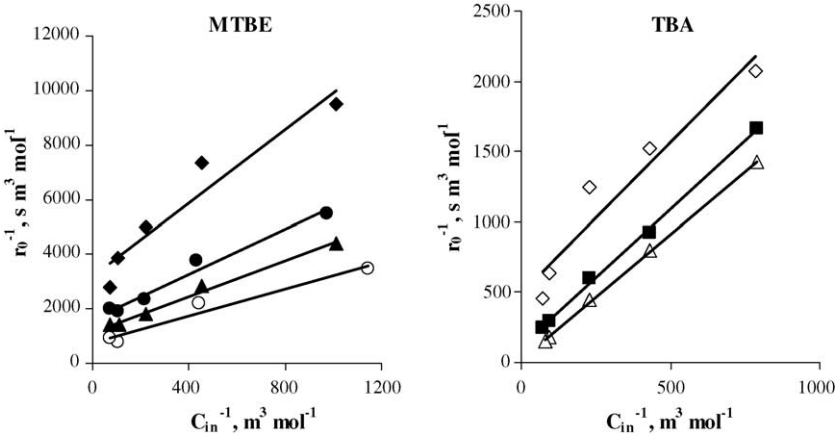

Fig. 3. Reciprocal TO reaction rates on TiO_2 vs. the reciprocal MTBE and TBA concentrations at: (◆) 388 K, (◇) 393 K, (●) 403 K, (■) 413 K, (▲) 418 K, (○) 433 K, (△) 453 K.

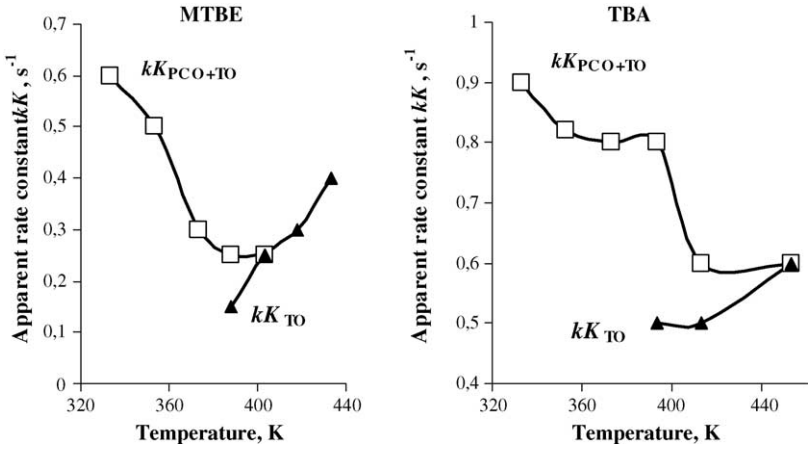

Fig. 4. Apparent reaction rate constant kK of PCO and TO of MTBE and TBA on TiO_2 vs. temperature.

increasing temperature, and thus with increasing reaction rate. This may be explained with the faster deterioration of adsorption compared with the chemical reaction rate growth with temperature. The TO contributed to the overall decomposition of MTBE and TBA, when applied simultaneously with PCO, ruling out PCO entirely at higher temperatures (Fig. 4). The overlapping points on the plots indicate the negligible role of PCO in the PCO/TO combination at the corresponding temperature: both VOCs were converted to 2-MP, no acetone was observed.

The numbers of the reaction rate constants k, the Langmuir adsorption coefficients K and the apparent rate constants kK at different temperatures are presented for both PCO/TO and TO reactions in Tables 1 and 2, respectively. The temperature interval for PCO in Table 1 partially overlaps the range in which TO takes place. Comparison of the two tables gives information about the contribution of TO to the PCO/TO reaction.

One can see that reaction rate constants k and the reaction rate for TO and PCO/TO of TBA are higher than that for MTBE, although the adsorption coefficients K are greater for MTBE. This indicates that a high surface concentration does not necessarily mean better PCO or TO performance: the reaction rate is not controlled by adsorption.

The values of constants for MTBE obtained in this study may be compared with the ones reported by Alberici and Jardim [8]: the apparent rate constant kK for PCO of MTBE with a black light lamp (30 W) at 323 K was reported as 0.031 s^{-1}, which is about 20 times lower than the number obtained for 333 K in the present study. This cannot be explained by the difference in the light intensities or the amount of the photocatalyst applied: Alberici and Jardim applied 3.2 mg TiO_2 cm^{-2} at the light flux 7.56×10^{-9} Einsteins cm^{-2} s^{-1} (the light tube surface was not coated with TiO_2). Our reactor with 1.4 mg TiO_2 cm^{-2} was irradiated with a 15 W luminescent lamp emitting in the same UV range at a light flux of about 1.8×10^{-9} Einsteins cm^{-2} s^{-1} (the light tube surface coated with TiO_2). The reference study was carried out with an inlet MTBE concentration as high as 605 ppmv at the stabilisation time of the reaction as long as 60 min. In our study, however, we noticed a dramatic decrease in the catalytic activity of TiO_2 at temperatures below 373 K. We thus observed the reported apparent reaction rate constants for only the first 20 min of the experimental run on relatively clean photocatalyst surface. The presence of 23% relative humidity (RH) reported in the reference paper (although with no temperature data for the RH reading) also differs from the conditions applied in the present study.

3.3. Photocatalyst lifetime

No catalyst deactivation was observed in the experiments at temperatures above 373 K for both VOCs and for both

Table 1
Reaction rate constants and Langmuir adsorption coefficients for photocatalytic oxidation (PCO/TO) of MTBE and TBA on TiO_2

T (K)	MTBE			TBA		
	K (m^3 mol^{-1})	k (mmol m^{-3} s^{-1})	kK (s^{-1})	K (m^3 mol^{-1})	k (mmol m^{-3} s^{-1})	kK (s^{-1})
333	3500 ± 700	0.20 ± 0.05	0.6 ± 0.1	730 ± 140	1.20 ± 0.2	0.9 ± 0.2
353	1600 ± 200	0.30 ± 0.04	0.5 ± 0.06	650 ± 15	1.30 ± 0.03	0.82 ± 0.002
373	580 ± 10	0.55 ± 0.01	0.3 ± 0.01	400 ± 15	1.90 ± 0.06	0.80 ± 0.002
388	490 ± 30	0.60 ± 0.01	0.25 ± 0.05	–	–	–
393	–	–	–	370 ± 50	2.10 ± 0.07	0.80 ± 0.002
403	400 ± 50	0.60 ± 0.01	0.25 ± 0.01	–	–	–

Table 2
Reaction rate constants and Langmuir adsorption coefficients for thermal oxidation of MTBE and TBA on TiO_2

T (K)	MTBE			TBA		
	K (m^3 mol^{-1})	k (mmol m^{-3} s^{-1})	kK (s^{-1})	K (m^3 mol^{-1})	k (mmol m^{-3} s^{-1})	kK (s^{-1})
388	490 ± 30	0.30 ± 0.03	0.15 ± 0.01	–	–	–
393	–	–	–	370 ± 50	1.6 ± 0.2	0.5 ± 0.1
403	400 ± 50	0.60 ± 0.01	0.25 ± 0.01	–	–	–
413	–	–	–	67 ± 1	7 ± 1	0.5 ± 0.1
418	350 ± 10	0.90 ± 0.01	0.30 ± 0.01	–	–	–
433	310 ± 10	1.3 ± 0.05	0.40 ± 0.02	–	–	–
453	–	–	–	10 ± 1	50 ± 1	0.6 ± 0.1

Table 3
Arrhenius equation parameters for the photocatalytic oxidation (PCO) and thermal oxidation (TO) of MTBA and TBA on TiO_2

Reaction	Parameter	MTBE	TBA
PCO			
MTBE from 333 to 373 K	ΔH (kJ mol^{-1})	−38 ± 1	−15 ± 2
TBA from 333 to 373 K	A_{ads} (m^3 mol^{-1})	0.003 ± 0.002	4.0 ± 0.5
	E (kJ mol^{-1})	27 ± 1	11 ± 2
	A_r (mol m^{-3} s^{-1})	3.0 ± 0.1	0.07 ± 0.01
TO			
MTBE from 388 to 433 K	ΔH (kJ mol^{-1})	−13 ± 1	−82 ± 1
TBA from 393 to 453 K	A_{ads} (m^3 mol^{-1})	7.43 ± 0.02	$(3.6 \pm 0.06) \times 10^{-9}$
	E (kJ mol^{-1})	45 ± 1	83 ± 1
	A_r (mol m^{-3} s^{-1})	250 ± 5	$(2.2 \pm 0.03) \times 10^{8}$

reactions—PCO/TO and TO. However, at temperatures below this level loss in the catalyst activity was observed (Fig. 5). The deactivation percent is defined as the relative decrease in the difference between the VOC concentrations in the inlet and the outlet streams after 150 min of reaction. *tert*-Butyl alcohol, in general, induced smaller deactivation of TiO_2 than MTBE: at 333 K MTBE totally clogged the catalyst with its oxidation by-products at an MTBE inlet concentration from 100 to 200 ppmv in 150 min. *tert*-Butyl alcohol under analogous conditions impeded just 50% of the catalyst activity. *tert*-Butyl alcohol did not clog the catalyst surface entirely in 150 min even at concentrations as high as 300 ppmv.

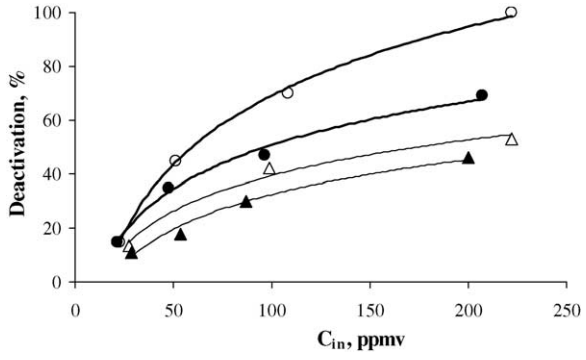

Fig. 5. Dependence of the TiO_2 deactivation in 150 min for PCO on MTBE and TBA inlet concentrations: MTBE at (○) 333 K and (●) 353 K, and TBA at (△) 333 K and (▲) 353 K.

4. Thermodynamics of PCO and TO

The dependence of the L–H kinetic parameters, the reaction rate constant and the Langmuir adsorption coefficient on temperature was analysed in the form of Arrhenius equations:

$$k = A_r e^{-E/RT} \quad (9)$$

$$K = A_{ads} e^{-\Delta H/RT} \quad (10)$$

where A_r and A_{ads} are pre-exponential factors for the reaction rate constant and the adsorption coefficient, mol m^{-3} s^{-1} and m^3 mol^{-1}, respectively; E and ΔH are the activation energy of the reaction and the adsorption enthalpy, kJ mol^{-1}; R is the universal gas constant, kJ mol^{-1} K^{-1} and T is temperature, K.

The numbers of the pre-exponential factors, the activation energy of the reaction and the adsorption enthalpy determined in the present study are given in Table 3. The PCO rate constant for MTBE appears to be more sensitive to temperature change than for TBA since it has larger Arrhenius equation parameters. The thermal decomposition reaction rate constant for TBA was more sensitive to the temperature variations.

5. Conclusions

The present research established the form of the kinetic description and the dependence of its parameters on temperature for the photocatalytic (PCO) and thermal (TO) oxidation of oxygenated motor fuel additives, methyl *tert*-butyl ether (MTBE) and *tert*-butyl alcohol (TBA).

Photocatalytic oxidation products for MTBE and TBA included acetone, carbon dioxide, and water; TO products of MTBE included 2-methyl-1-propene (2-MP), carbon monoxide, carbon dioxide, and water; TBA thermal decomposition products were limited to 2-MP and water.

The photocatalyst demonstrated stable activity at temperatures above 373 K, but partially lost its activity at lower temperatures. The authors explain such behaviour by the partial occupation of the TiO_2 adsorption sites with oxidation by-products.

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