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Kinetic study on catalytic methane esterification in oleum catalyzed by iodine

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ABSTRACT

The direct and selective oxidation of methane to methyl bisulfate in oleum is reported. Iodine is used as a catalyst. In order to optimize the process the initial methane pressure, oleum concentration and temperature are varied. The reaction is first order with methane pressure and sulfur trioxide concentration. The rate of the ester production is defined by the empirical equation in the temperature range 80–180 °C, methane pressure 1–5 MPa, sulfur trioxide concentration 0–5.95 mol dm^{-3}, time 0–20 h. The equation fits the experimental data well. The apparent activation energy of methane oxidation in oleum with iodine as a catalyst is found to be equal to 44.8 ± 1.2 kJ mol^{-1}.

1. Introduction

Despite being the most abundant and least expensive hydrocarbon feedstock available, methane, is rarely used as chemical building blocks because few viable methods exist for its direct conversion into valuable products. Methanol, for example, is not produced directly by oxidation of methane, but by high-temperature, energy-intensive steam reforming and subsequent hydrogenation processes, which date back to the 1920s.

Since 1990, the study of catalytic system for selective oxidation of CH_4 has already evolved from a traditional heterogeneous catalysis into a new system involving the homogenous catalysis, metal coordination complex, and achieved a great step forward.

Kao et al. [1] suggested a homogenous catalytic system using a salt of Pd(II) as a catalyst and H_2O_2 as an initiator in CF_3COOH medium. The trifluoroacetic acid was first oxidized to trifluoroperacetic acid. Then reaction between methane and trifluoroperacetic acid was catalyzed by Pd(II) and methyl ester of trifluoroacetic acid was obtained. The ester can be hydrolyzed to produce methanol. At temperature equal to 80 °C and 5.5 MPa of methane pressure the once-through yield of CH_3OH may reach about 60%.

Periana et al. [2] suggested other homogeneous catalytic system using Hg(II) salt as catalyst in fuming sulfuric acid. The reaction took place at 180 °C and 3.45 MPa methane pressure. The methane was oxidized to methyl bisulfate. CH_3OSO_3H was further hydrolyzed to produce methanol. The methane conversion equal to 50% and selectivity to ester equal to 85% was achieved.

Gang et al. [3] applied similar catalytic system as Periana's group [2] but fuming sulfuric acid was more concentrated (65 wt% SO_3). The methane oxidation was studied at a temperature range of 150–200 °C and a methane pressure range of 4–10 MPa. The analysis of pressure–time relationship of the system led to information about reaction rate.

Platinum complex catalyst in fuming sulfuric acid (20 wt%) was reported by Periana et al. [4] for the direct, oxidative conversion of methane to ester at greater than 70% one-pass yield based on methane. The reaction was performed at 180 °C and 3.45 MPa methane pressure. The catalysts were platinum complexes derived from the bidiazine ligand family that were stable, active, and selective for the oxidation of a carbon–hydrogen bond of methane to produce methyl esters.

Gang et al. [5] applied a new series of iodine-containing compounds as catalysts for the selective oxidation of methane to methyl sulfates in oleum (65 wt% SO_3). A mathematical model for the relationship between the initial reaction rate and the iodine concentration and methane pressure has been given. In authors' opinion suitable reaction temperatures are in the range 170–190 °C at methane pressure 4 MPa. The selectivity of methane to methyl sulfates was found to be ca. 92% and ester yield 70%.

Periana et al. [6] applied similar catalytic system as Gang's group [5] but they used iodine dissolved in sulfuric acid containing only 0.5–3% SO_3. Several experiments have been made at 195 °C and methane pressure 3.4 MPa.

In present work, the kinetics of the methane functionalization by iodine in oleum (up to 25 wt% SO_3) is studied. The systematic experimental steps are applied to the study of the relationship between the initial reaction rate and concentration of sulfur trioxide, methane partial pressure and temperature. The obtained

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equation is applicable for the estimation of the reaction rate and the ester concentration in any moment of the process up to 20 h.

Periana et al. [6] and Gang et al. [5] have used iodine in oleum. The first ones used week oleum (≤2.5 wt% SO_3) but high temperature (195 °C). The focus of their work was the reaction mechanism and not optimization of the process. The last ones carried detailed research including kinetics but they used much more concentrated oleum (65 wt% SO_3) and temperature 170–190 °C.

In an industrial process based on the above-mentioned method it would be very important to use oleum containing not much sulfur trioxide. The low temperature would be an advantage as well.

2. Experimental and methods

2.1. The chemicals used

Oleum, 25 wt% SO_3 (5.95 mol dm^{-3} SO_3) Zaklady Azotowe Tarnow, Poland CH_4, 2.5 (99.5%), Messer platinum chloride ($PtCl_4$), Merck iodine, purum p.a., ≥99.5% Fluka.

2.2. The reactor

The methane functionalization was conducted in a PTFE-lined stainless steel autoclave with a capacity of 0.25 dm^3. The volume of the reaction region (oleum volume) was 0.1 dm^3. The reactor was equipped with a magnetic stirrer. The autoclave was heated on the outer wall and a PID temperature controller controlled the temperature. An electronic pressure sensor was connected to measure the gas pressure inside the reactor. A computer recorded the pressure and temperature data automatically. The pressure–time and temperature–time graphs were displayed on a PC simultaneously.

Due to the values of the pressure applied in the experiments (up to 6.77 MPa), the van der Waals equation of the states was used for the calculations.

2.3. Product identification

The identification of the reaction products in the liquid state was done using natural abundance ^{13}C NMR measurements performed on a Bruker DPX 400 spectrometer. DMSO-d_6 was used as an external lock and a reference. The dimethyl sulfate was identified as the only one organic liquid product. The procedure identification of ester in oleum is described in detail in ref. [7]. After treatment with water the ester was analyzed quantitatively as methanol by gas chromatography. The analysis for gases was carried out by gas chromatography as well.

2.4. The process

The iodine was used as the catalyst of the methane functionalization. It was found by us and other authors [3,7] that the ester yield increases when the concentration of catalyst is increased up to saturation point. Beyond this point, increasing the catalyst concentration will not cause further increases of the yield. In our investigations the saturated solution of catalyst in oleum was used. The process was carried out at 60–180 °C. The methane partial pressure was varied from 1 to 6.77 MPa. The sulfur trioxide concentration in oleum ranged from 0 to 5.95 mol dm^{-3}. The experiments lasted up to 20 h.

The saturated solution of iodine in oleum was sealed in the autoclave. The reactor was heated to the reaction temperature and then pressurized with methane to the desired pressure. The process was terminated by stopping the heating, and cooling down the reactor with water.

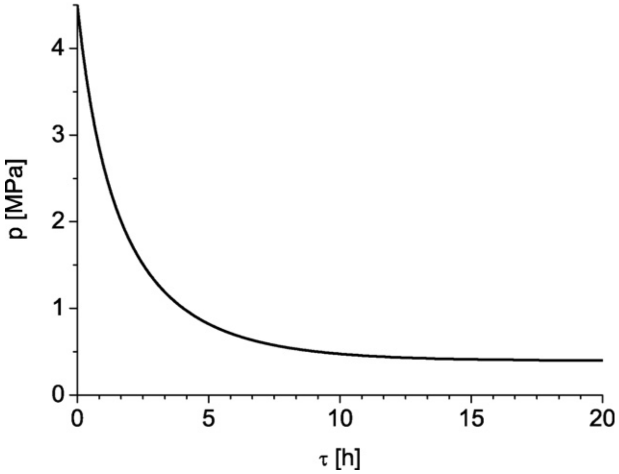

Fig. 1. The pressure in the reactor vs. reaction time. Initial methane pressure = 4.27 MPa; temperature = 160 °C; SO_3 concentration = 5.95 mol dm^{-3}.

3. Results and discussion

We have found that the following reactions took place:

$$CH_4 + SO_3 + H_2SO_4 \rightarrow CH_3OSO_3H + SO_2 + H_2O$$

$$CH_4 + 4SO_3 \rightarrow CO_2 + 4SO_2 + 2H_2O$$

$$H_2O + SO_3 \rightarrow H_2SO_4$$

Fig. 1 shows a typical plot of pressure in the reactor versus reaction time from the point when the methane is pressurized up to point when cooling stops the reaction. We did not give consideration to initial stages: heating, pressurizing and ending stage: cooling. After the reactor is pressurized with CH_4 the pressure starts dropping rapidly because methane and sulfur trioxide is consumed, and the producing sulfur dioxide is dissolved in the oleum. After 5 h pressure is lowered about 80%. Then pressure falls down 9% after next 5 h and only 1% after next 10 h. The pressure fall is induced mainly by methane oxidation. The pressure decrease due to sulfur trioxide consuming would be about 3% if 100% of methane reacted. The major if not the sole product of the methane oxidation is methyl bisulfate. No dimethyl sulfate was detected by ^{13}C NMR method. The traces of carbon dioxide were found in resultant gas mixture. The CO_2 yield was below 1%. Taking into consideration methane and sulfur trioxide consumption and products of the oxidation, on the basis of Fig. 1 one can calculate methane conversion and methyl bisulfate concentration in oleum values in any moment of the process.

The experiments were carried up to 20 h. The initial methane pressure, oleum concentration and temperature were varied. The methane conversion and ester concentrations were analyzed as described above (by GC) and calculated theoretically from the overall pressure drop taking into considerations mass balance and the chemical equations. Fig. 2 shows the predicted (C_E^{pre}) versus observed (C_E^{obs}) values of ester concentrations. The small difference (no higher than 5%) between experimental results and theoretical calculations indicates that the value of pressure drop can be used for the methane conversion and ester yield (or concentration) estimation. The analysis of the reaction mixture is not necessary.

It is worth saying that this process involves mass transfer of one or more species from the gaseous phase to the liquid phase. In the liquid phase methane from the gas phase is converted by a chemical reaction with sulfur trioxide already present in the liquid phase. The phenomenon of gas–liquid mass transfer is not new and has been intensively studied by scientists in the past (the stagnant film

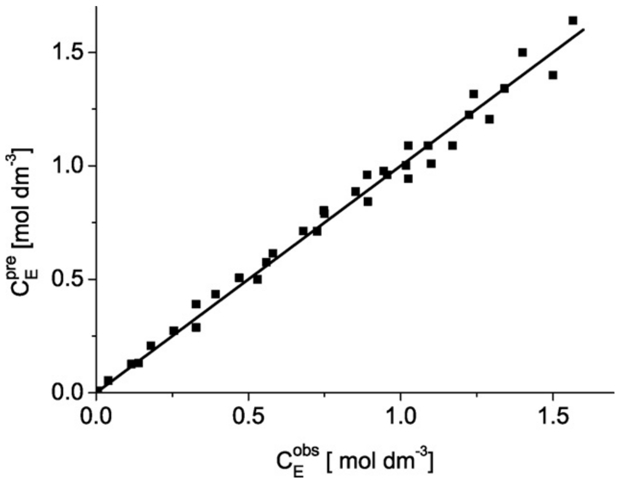

Fig. 2. Ester concentration calculated theoretically from the overall pressure drop vs. observed ester concentration. (■) Ester concentration and (—) $y = x$.

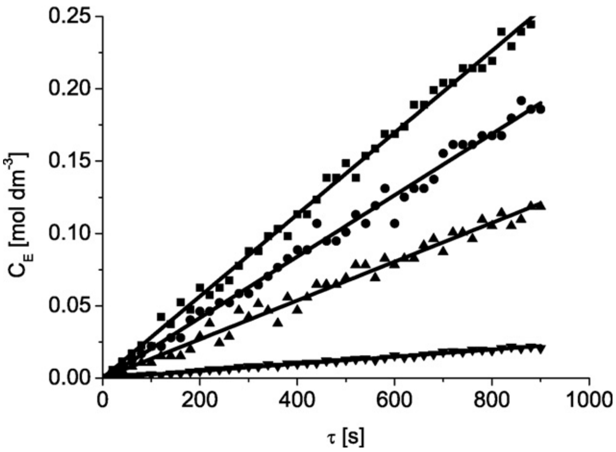

Fig. 3. Ester concentration vs. time. Methane pressure = 2.27 MPa, temperature = 160 °C, SO_3 concentration: (■) 5.95 mol dm^{-3}, (●) 4.33 mol dm^{-3}, (▲) 2.65 mol dm^{-3} and (▼) 0.45 mol dm^{-3}.

model was first described in 1923 [8]). Despite this, it was concluded that some phenomena of gas–liquid mass transfer can be regarded as nearly completely unexplained. The aim of this work is not to study some of these phenomena but to find the reasonably useful equations for the reactor design calculations.

If concentration of catalyst (saturated solution hire) is constant, the rate of the ester formation depends on methane partial pressure, sulfur trioxide concentration in oleum and temperature. Therefore the reaction rate (r) equation in this system is postulated as follows:

$$\frac{dC_E}{dt} = r = r_{(T)} \cdot r_{(SO_3)} \cdot r_{(p_{CH_4})} = f_0(T) \cdot f_1(C_{SO_3}) \cdot f_2(p_{CH_4}) [\mathrm{mol\,dm^{-3}\,s^{-1}}] \tag{1}$$

where C_E, C_{SO_3} are the methyl bisulfate, sulfur trioxide concentrations [mol dm^{-3}]; p_{CH_4} the methane partial pressure [MPa]; $r_{(T)} = f_0(T)$ the function of the temperature in the reaction rate equation; $r_{(SO_3)} = f_1(C_{SO_3})$ the function of the sulfur trioxide concentration in the reaction rate equation; $r_{(p_{CH_4})} = f_2(p_{CH_4})$ is the function of the methane partial pressure in the reaction rate equation.

In order to investigate the influence of the sulfur trioxide concentration in oleum on the methyl bisulfate concentration, the initial concentration of SO_3 was varied while keeping every other parameter constant (such as: methane pressure, 4.27 MPa; temperature, 160 °C). It was observed that for the first 15 min the ester concentration exhibited a linear dependence with time with regression coefficient better than 0.9. The initial rates values were calculated from regression slopes determined over this time interval for each sulfur trioxide concentration. An example of the results obtained is given in Fig. 3 and shows wholly typical trends.

Fig. 4 illustrates the initial rates calculated from linear fittings as a function of sulfur trioxide concentration.

The reaction rate is directly proportional to sulfur trioxide concentration at constant temperature and methane pressure. The slope of $r = f_1(C_{SO_3})$ is equal to $5.38 \pm 0.24 \times 10^{-5}$ and y-intercept is $0.179 \pm 0.091 \times 10^{-5}$. The regression coefficient is equal to 0.98. On the basis of a positive value for the y-intercept one could conclude that ester was obtained in 100% sulfuric acid instead of oleum. It was found that in 100% sulfuric acid methane transformation does take place but reaction is very slow—about hundred times slower than in oleum of 5.95 mol dm^{-3}.

Eq. (2) can be used to calculate the rate of ester production at temperature 160 °C and methane partial pressure 4.27 MPa.

$$r = f_1(C_{SO_3}) = 5.38 \times 10^{-5} C_{SO_3} + 0.179 \times 10^{-5} \tag{2}$$

The effect of methane partial pressure was investigated between 1 and 7.22 MPa while keeping temperature and sulfur trioxide concentration at 160 °C and 5.95 SO_3 mol dm^{-3}, respectively. It was observed that for the first 15 min the ester concentration exhibited a linear dependence with time with regression coefficient better than 0.9. The initial rate values were calculated from regression slopes. Results for 5.27, 3.67, 2.27 and 1.00 MPa are plotted in Fig. 5. Similar trends for all other methane partial pressures revealed identical trends and are not therefore given in this report.

The reaction rate was found to be a function of the methane partial pressure and SO_3 concentration in oleum (Eq. (1)). The influence of sulfur trioxide concentration has been eliminated by plotting rates observed at different pressures divided by rate obtained at partial pressure of methane equal to 4.27 and with sulfur trioxide concentration equal to 5.95 mol dm^{-3} ($r_{4.27,5.95}$).

Fig. 6 gives the variation of rate due to methane partial pressure at 160 °C and with SO_3 concentration equal to 5.95 mol dm^{-3}. Below 1 MPa methyl bisulfate was not found in the resultant liquid mixture. The absence of the ester may have been a result of low methane concentration in oleum at low pressure. A strong positive effect is apparent when methane partial pressure is varied from 1 to 5 MPa. Above 5 MPa the positive effect is weaker. The reason for the slowing rate is that the solubility of non-ideal real gas at high pressure is not proportional to partial pressure of this gas. The

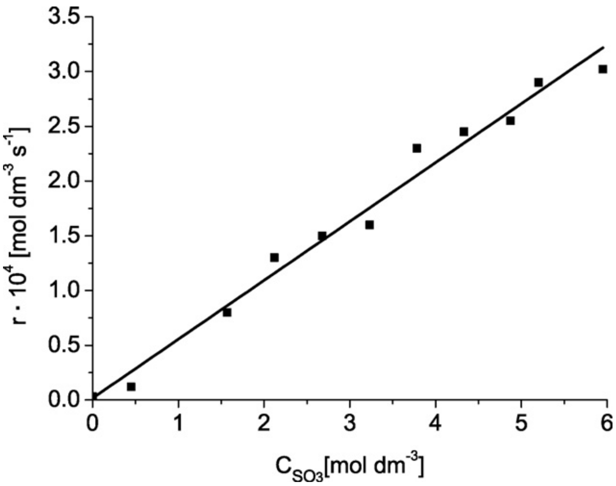

Fig. 4. Initial reaction rate vs. sulfur trioxide concentration. Methane pressure = 4.27 MPa and temperature = 160 °C.

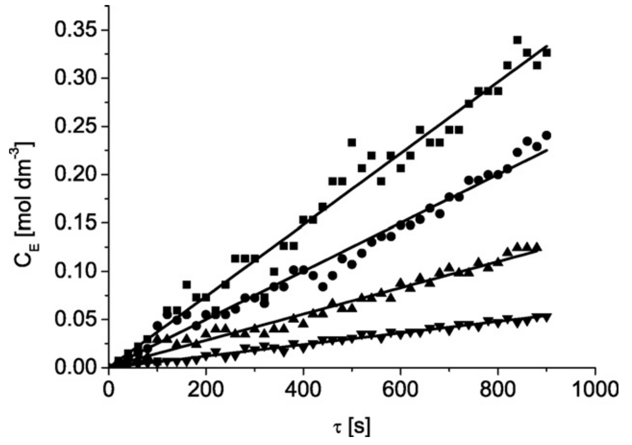

Fig. 5. Ester concentration vs. time. SO_3 concentration 5.95 SO_3 mol dm^{-3}, temperature 160 °C, methane pressure: (■) 5.27 MPa, (●) 3.67 MPa, (▲) 2.27 MPa and (▼) 1.00 MPa.

Henry's law cannot be used for the calculations. In the region from 1 to 5 MPa the mass transfer is fast and the rate of the ester productions is kinetically controlled. Above 5 MPa chemical reaction is faster then rate of dissolution of methane in oleum.

On the basis of Fig. 6 one can state that in the kinetics region the rate of the ester production is directly proportional to the methane partial pressure. The slope of $r = f_2(p)$ is equal 0.254 ± 0.008 and y-intercept -0.0836 ± 0.0281. The regression coefficient is equal to 0.98. The negative value for the y-intercept indicates that ester cannot be obtained if the methane is present in the reactor but the methane partial pressure is too low. We observed this phenomenon.

Eq. (3) can be applied to calculate the rate of ester production at temperature 160 °C and with SO_3 concentration equal to 5.95 mol dm^{-3}.

$$r = f_2(p_{\mathrm{CH_4}}) = 0.245 p_{\mathrm{CH_4}} - 0.0836 \quad (3)$$

Taking into account Eqs. (2) and (3) the reaction rate is described by the formula (4) as a function of the sulfur trioxide concentration and the methane partial pressure.

$$r = f(C_{\mathrm{SO_3}}, p_{\mathrm{CH_4}}) = 1.37 \times 10^{-5}(C_{\mathrm{SO_3}} + 0.0333)(p_{\mathrm{CH_4}} - 0.329) \quad (4)$$

Eq. (4) was found empirically and can be applied at 160 °C when sulfur trioxide is varied from 0 to 5.95 mol dm^{-3} and methane partial pressure from 1 to 5 MPa.

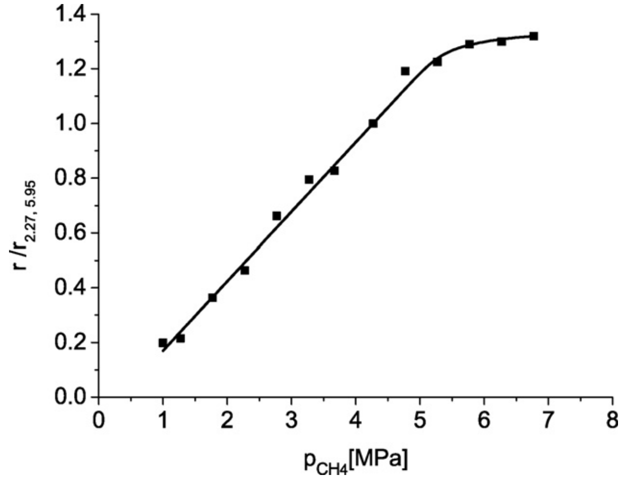

Fig. 6. Relative reaction rate as a function of methane partial pressure. SO_3 concentration 5.95 mol dm^{-3}, temperature 160 °C.

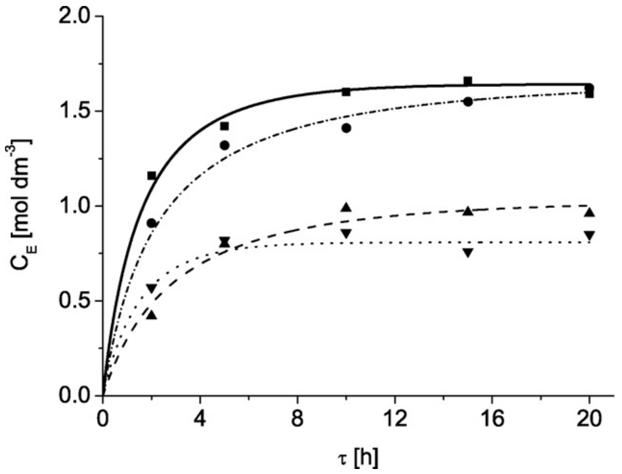

Fig. 7. The experimental and theoretical values of the ester concentration vs. time. Temperature 160 °C; $C_{\mathrm{SO_3}} = 5.95$ mol dm^{-3}, $p_{\mathrm{CH_4}} = 4.27$ MPa: (■) experimental values, (—) theoretical calculations; $C_{\mathrm{SO_3}} = 3.27$ mol dm^{-3}, $p_{\mathrm{CH_4}} = 5.27$ MPa: (●) experimental values, (·-·) theoretical calculations; $C_{\mathrm{SO_3}} = 2.01$ mol dm^{-3}, $p_{\mathrm{CH_4}} = 4.27$ MPa: (▲) experimental values, (- - -) theoretical calculations; $C_{\mathrm{SO_3}} = 5.95$ mol dm^{-3}, $p_{\mathrm{CH_4}} = 2.27$ MPa: (▼) experimental values, (···) theoretical calculations.

After replacing the instant concentration of SO_3 and the instant CH_4 partial pressure at a certain time with their initial values Eq. (5) was found:

$$r_{t=160\,^\circ\mathrm{C}} = 1.37 \times 10^{-5}(C_{0\mathrm{SO_3}} - 2C_\mathrm{E} + 0.033) \times \left(\left(p_{0\mathrm{CH_4}} - \frac{0.360C_\mathrm{E}}{0.150 - 0.00428C_\mathrm{E}} + 0.0982C_\mathrm{E}\right) - 0.329\right) \quad (5)$$

where $C_{0\mathrm{SO_3}}$ is the initial SO_3 concentration in oleum [mol dm^{-3}]; $p_{0\mathrm{CH_4}}$ is the initial methane partial pressure [MPa].

By numerical integration of Eq. (5) one can calculate the theoretical values of the ester concentration. In order to find out the agreement between theoretical and experimental data, additional experiments were carried out in which the time was varied from 2 to 20 h.

The theoretical and experimental values of the ester concentration versus time at temperature 160 °C are presented in Fig. 7. The sulfur trioxide concentration and methane partial pressure were varied. Based on the data presented in Fig. 7 one can see that the experimental results show very good agreement with the theoretical predictions. The calculated values are in excellent agreement with that obtained from measurements. The differences between the theoretical predictions and the experimental results were lower than 7%.

Although, in Eq. (5) the factor 0.360 already contains the value of the temperature ($0.360 = 0.00083 \cdot T$) but it follows from the van der Waals equation. It is just a way to express the instant methane partial pressure in the reactor as a function of the ester concentration.

The function of the temperature in the reaction rate equation ($r(T) = f_0(T)$) is expressed by the specific reaction rate coefficient and of course the influence of temperature is described by the Arrhenius equation. From Eq. (5) it was found that the reaction rate coefficient at temperature 160 °C is equal to 1.37×10^{-5} s^{-1} MPa^{-1}.

The influence of temperature on the initial reaction rate was investigated at isothermal conditions. The temperature was varied from 60 to 180 °C while keeping methane pressure and sulfur trioxide concentration at 4.27 MPa and 5.95 mol dm^{-3}, respectively. The dependence of the reaction rate on the temperature is shown in Fig. 8. Methane oxidation does not occur up to 60 °C. Therefore, the lowest temperature at which methyl bisulfate was observed was 60 °C.

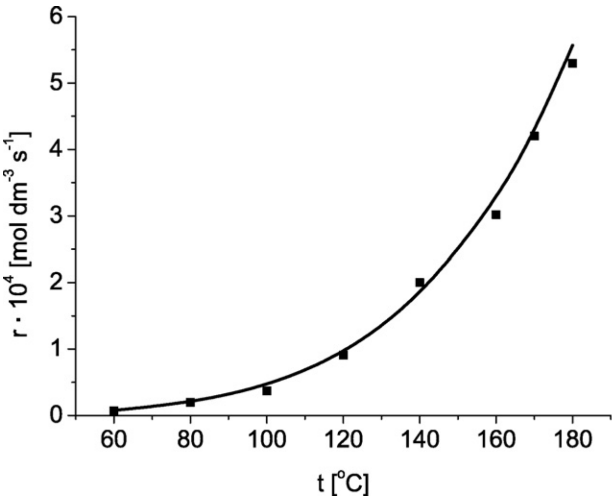

Fig. 8. Initial reaction rate vs. temperature. Methane pressure = 4.27 MPa and SO_3 concentration = 5.95 mol dm^{-3}.

Table 1
The dependence of the reaction rate coefficient on the temperature.

Temperature [°C]	k (×10^6) [MPa^{-1} s^{-1}]
60	0.32
80	0.90
100	1.67
120	4.11
140	9.04
160	13.65
170	18.99
180	23.96

The reaction rate coefficient at each temperature was determined by Eq. (6).

$$k=\frac{k_{160}}{1.37\times10^{-5}(C_{0SO_3}-2C_E+0.033)((p_{0CH_4}-(0.360C_E/(0.150-0.00428C_E))+0.0982C_E)-0.329)} \qquad (6)$$

where k_{160} is the value of the reaction rate at temperature 160 °C. The values of the reaction rate coefficient are listed in Table 1.

In order to find energy activation value the natural log of that rate constants versus the reciprocal of temperature in Kelvin were plotted (Fig. 9). A straight line was obtained, with a slope of −5450 ± 130. Therefore, the apparent activation energy of methane oxidation in oleum with iodine as a catalyst was found to be 45.3 ± 1.1 kJ mol^{-1}.

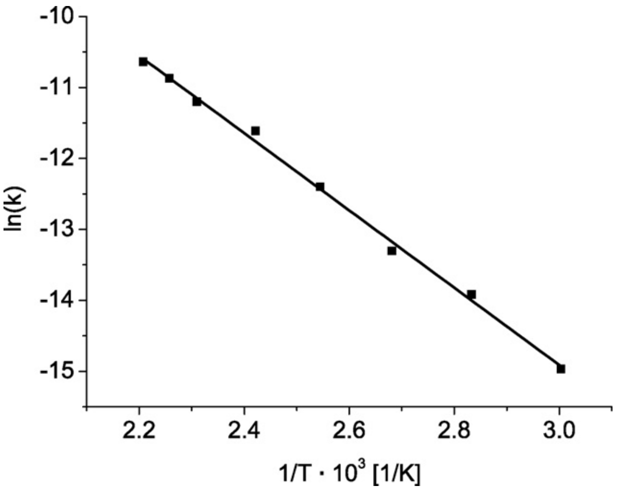

Fig. 9. The Arrhenius plot.

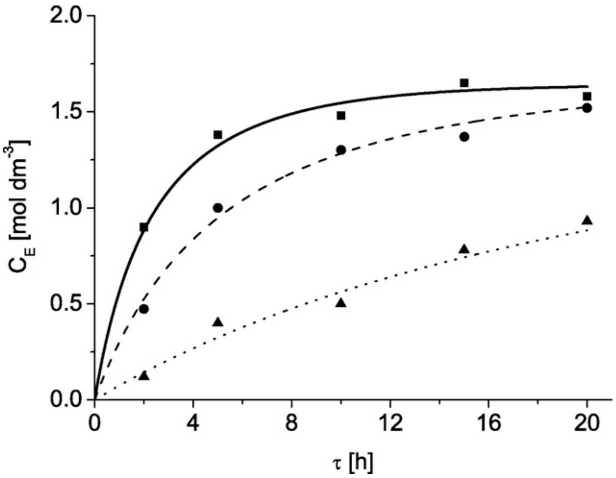

Fig. 10. The experimental and theoretical values of the ester concentration vs. time. SO_3 concentration = 5.95 mol dm^{-3}, methane pressure = 4.27 MPa; temperature = 140 °: (■) experimental values, (—) theoretical calculations; 120 °C: (●) experimental values, (- - -) theoretical calculations; 80 °C: (▲) experimental values, (· · ·) theoretical calculations.

Only apparent energy activation can be calculated because of difficulties in the estimation of the methane concentration in oleum. It is not possible to find the dependence of methane concentration in oleum over pressure $C_{CH_4}=f(P_{CH_4})$ [9]. If it would be possible to replace methane pressure in Eq. (6) by function $C_{CH_4}=f(p_{CH_4})$ one would be able to calculate the true energy activation. The value of methane energy of solubility influences on the value of apparent energy activation calculated from the Arrhenius plot.

Finally Eq. (7) defining the reaction rate as a function of temperature, sulfur trioxide concentration and methane pressure was obtained.

$$r=k_T(C_{0SO_3}-2C_E+0.033)\times\left(\left(p_{0CH_4}-\frac{0.360C_E}{0.150-0.00428C_E}+0.0982C_E\right)-0.329\right) \qquad (7)$$

By numerical integration of Eq. (7) the theoretical values of the ester concentration were calculated at temperature 80, 120, 140 °C and time up to 20 h. The theoretical and experimental values of the ester concentration versus time are presented in Fig. 10. Based on the data presented in Fig. 10 one can see that the experimental results show very good agreement with the theoretical predictions.

4. Conclusions

The ester production from methane and oleum when iodine is used as a catalyst is controlled kinetically up to 5 MPa. The reaction is first order with methane pressure and sulfur trioxide concentration. A positive effect of the methane partial pressure and a sulfur trioxide concentration on the rate is evident. The strength of the effect for methane pressure depends on the methane pressure value. The rate of the ester production is defined by the empirical Eq. (7) in the temperature range 80–180 °C, methane pressure 1–5 MPa, sulfur trioxide concentration 0 – 5.95 mol dm^{-3}, time 0–20 h. Eq. (7) fits the experimental data well and is a step towards the mass production of the methyl bisulfate on an industrial scale. The Arrhenius plot was linear allowing apparent activation energy to be calculated. The apparent activation energy of methane oxidation in oleum with iodine as a catalyst is equal to 44.8 ± 1.2 kJ mol^{-1}.

Acknowledgment

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