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Electrochemical study of catalytic oxidation of naphthalene in molten sulphate pyrosulphate at 425° C with vanadium pentoxide

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Naphthalene oxidation in a molten mixture of potassium sulphate pyrosulphate at 425° C in the presence of vanadium pentoxide takes place in three stages. The electrochemical study of each stage has led to the proposal of kinetic equations for the initial rates:

(i) naphthalene oxidation by the medium

$$V_1^0 = 2 \times 10^{-2} P_{C_{10}H_8}$$

(ii) mixture regeneration by V_2O_5

$$V_2^0 = 19.2 \times 10^{-2} P_{SO_2}$$

(iii) catalyst regeneration by oxygen

$$V_3^0 = 82.8 P_{O_2} [V(IV)]^2$$

This shows that the molten salt acts not only as a solvent but also as a reagent in the catalytic process.

Nomenclature

E_S^0	S(VI)/S(IV) couple normal potential = 0.240 V/Ag–Ag_2SO_4
E_V^0	V(V)/V(IV) couple normal potential = 0.365 V/Ag–Ag_2SO_4
E^1	potential at initial time
$C^*_{SO_4}$	SO_4^{2-} ion solubility = 0.51 mol dm^{-3} [32]
$C^*_{O_2}$	oxygen solubility = 4.2×10^{-7} mol cm^{-3} [31]
K_L	mass transfer physical coefficient = 2.2×10^{-3} cm s^{-1} [27, 31]
K_D	proportionality coefficient between maximum current and SO_2 solubility = 1.13×10^{-3} mA dm^{-3} mol^{-1} [27]
a'	air exchange per unit of volume = 23×10^{-2} cm^{-1}
γ_{SO_2}	Henry's law constant for SO_2 = 0.2×10^{-2} dm^{-3} atm mol^{-1}
γ_{O_2}	Henry's law constant for O_2 = 2.3×10^5 cm^3 atm mol^{-1} [31].

1. Introduction

Much work concerning new applications of molten salts has been published during the last few years. Molten salts have been used for many centuries in metal extraction, glass manufacture and, more recently, in applications such as fused salt electrolysis. Usually dissociated into ions, molten salts are often good solvents for oxides, carbides, nitrides and metals. Their high thermal stability, low vapour pressure, good thermal and electrical conductivity and low viscosity may be expected to confer on them an increasing technological importance in the future [1].

Thus molten salts are used to find solutions to the following problems:

(i) The nuclear power industry produces large volumes of combustible waste contaminated with radioactive compounds. Combustion of such wastes in a molten salt reactor retains the radioactive compounds in the melts [2]. Greenberg [3] and Lessing [4] developed a commercial incinerator based on combustion in melts comprising mainly of sodium sulphate.

(ii) Rockwell [5] patented a process in which industrial, municipal and agricultural wastes were pyrolysed. Gas and char were formed and the latter was consumed by reaction with sulphate to give sulphite and carbon oxides.

The breadth of applications of molten salts in organic synthesis can be seen in very useful reviews by Sundermayer [6], by Kenney [1] and by Hatt [2].

A molten salt can have several roles in reaction media:

(i) as a direct fluid heat transfer medium for both exothermic and endothermic reactions;

(ii) as a solvent for reagent and/or reactant of reaction;

(iii) as a reagent that is chemically or electrochemically regenerated;

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(iv) as a consumable reagent;
(v) as a catalyst.

The use of a potassium sulphate–pyrosulphate mixture for naphthalene oxidation is described below. Naphthalene is mainly used for the production of phthalic anhydride by gas–solid heterogeneous catalytic oxidation [7, 8]. The most recently used catalysts are based on vanadium pentoxide with potassium sulphate used as a promotor, supported on silica or titanium oxide. Sulphur dioxide is often added to the air–naphthalene mixture to maintain the catalytic activity [9–13]. Foster [14] has shown that, for a 1 : 1 molar ratio of $SO_3 : K_2SO_4$, which corresponds to $K_2S_2O_7$ the catalyst selectivity for the formation of phthalic anhydride reaches a maximum.

Boreskov *et al.* [15, 16] confirmed the hypothesis of the liquid film on the surface of vanadium pentoxide industrial catalysts when they are associated with alkaline sulphates. Many authors and patents have used naphthalene oxidation in fused salt sulphates to produce phthalic anhydride [1, 18–26].

Taking all these factors into account, we used the eutectic mixture of K_2SO_4–$K_2S_2O_7$ containing 95% (by weight) of molten $K_2S_2O_7$. This medium, which has already been used [27–33], proved to be a good V_2O_5 solvent. It permits the approximate reconstitution of the liquid film on a macroscopic scale, with the advantage of a fair knowledge of the gas–liquid contact surfaces. Moreover, its fusion temperature is close to those used in solid–gas heterogenous catalysis [7, 8, 34].

Electrochemical studies of molten sulphates by Inman *et al.* [35], More [36] and Cutler [37], confirm our work on molten sulphate–pyrosulphate where traditional electrochemical methods are used.

2. The solvent

The K_2SO_4–$K_2S_2O_7$ mixture used has a melting point of 398°C and its density is $2.03 \pm 0.03\,g\,cm^{-3}$ [27], varying slightly with temperature and sulphate composition. At the working temperature (425°C), the equilibrium [38–40]:

$$S_2O_7^{2-}\ (liq) \rightleftharpoons SO_4^{2-}\ (sat) + SO_2\ (g)$$

has a constant $K_d = [SO_4^{2-}]P_{SO_2} = 10^{-2.7}$atm [27]. This equilibrium defines the acid–basic domain. According to Lux's terminology [41], acid is any species capable of fixing an O^{2-} ion and a base one which liberates an O^{2-} ion. In the case of molten pyrosulphate, addition of a base results in solid potassium sulphate which can be remelted by sulphur trioxide bubbling according to the following equilibrium:

$$K_2S_2O_7 + K_2O \rightleftharpoons 2K_2SO_4$$

$$K_2SO_4 + SO_3 \rightleftharpoons K_2S_2O_7$$

Thus, in molten pyrosulphate, any compound liberating sulphur trioxide is acid and any compound liberating an SO_4^{2-} ion is basic. Acidity is limited by an SO_3 pressure of 1 atm and basicity by a saturated solution of potassium sulphate. The solubility of K_2SO_4, determined by Pena [42] is 5.6×10^{-4} mol cm^{-3} which shows that the eutectic mixture, saturated with SO_4^{2-}, is a basic buffer medium.

The presence of water vapour over the liquid may be responsible for the transformation:

$$K_2S_2O_7 + H_2O \rightleftharpoons 2KHSO_4$$

This increases the number of acid–base reactions. Special caution regarding reactor tightness and gas purification is essential to eliminate water traces. The oxidizing properties of this molten salt are shown by its corrosive power in the presence of most metals [43–45]. All metals, except gold, undergo attack. Attack on platinum is minor giving two maxima on the potential–current curve, probably due to platinum oxidation to PtO and PtO_2 oxides.

3. Experimental details

Figure 1 shows schematically the entire apparatus

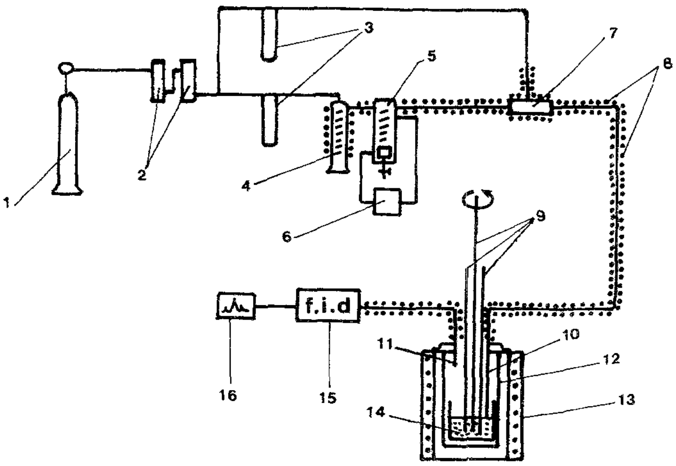

Fig. 1. The experimental set-up for the reaction and analysis of naphthalene oxidation in a K_2SO_4–$K_2S_2O_7$ eutectic mixture and in the presence of V_2O_5. (1) Gas (air–N_2), (2) silicagel, (3) flow meter, (4) naphthalene tank, (5) condenser, (6) thermostat, (7) mixer, (8) heat corder, (9) electrodes, (10) gas inlet, (11) gas outlet, (12) reactor, (13) oven, (14) molten salts, (15) chromatograph, (16) recorder.

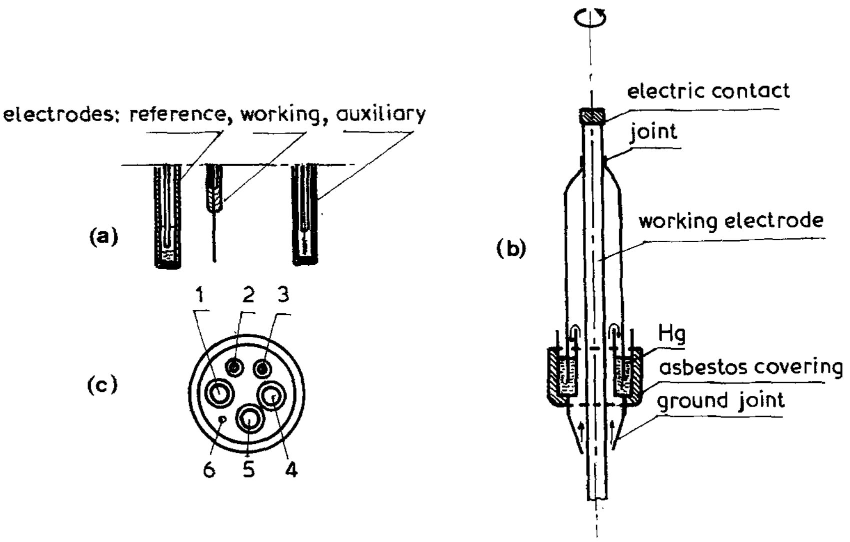

Fig. 2. (a) Electrodes; (b) diagram of rotating electrode; (c) lid of reactor: (1) auxiliary electrode, (2) gas outlet, (3) gas inlet, (4) working electrode (5) reference electrode, (6) finger for thermocouple.

used for the oxidation of naphthalene in molten potassium sulphate–pyrosulphate medium.

3.1. *Thermal apparatus*

The thermal apparatus consists of an oven containing a pot filled with a tin–lead mixture acting as a thermoregulator bath. All temperatures are referred to the various points on the assembly by means of chromel–alumel thermocoax thermocouples.

3.2. *Reaction vessel*

Kenney [1] recommends, for laboratory reactors, the use of inert materials with smooth walls. He proposes quartz and Pyrex as convenient materials at temperatures lower than 600° C for molten salt media with chloride, sulphate and pyrosulphate.

The tight Pyrex glass cell (Fig. 2c) has a lid which can be adapted by flat grinding and carries five conical ground joints to supply the reactor with gas, to remove the products and to introduce the three electrodes.

3.3. *Feeding the reactor*

Because of the hygroscopic nature of potassium sulphate, the gas flow (air, nitrogen), is previously dried and purified using columns containing sodium hydroxide, silicagel and molecular sieves. The flow is divided into two parts. The first circuit goes through a naphthalene tank, then into a condenser based on the model used by Germain [46] and Vanhove [47]. The naphthalene-saturated air (or nitrogen) leaves the condenser and enters a mixer into which air (or nitrogen) from the second circuit is also introduced. The gas mixture is then preheated before entering the reactor.

3.4. *Electrochemical apparatus*

Because of the particularly corrosive nature of the molten medium, platinum has been chosen for both working and auxiliary electrodes. The rotating working electrode consists of a 0.5 mm diameter platinum wire brazed on to a copper filament and partially inserted in glass. It is made steam-proof with mercury and rotates without friction (Fig. 2b). The auxiliary electrode has a spiral winding, which gives it a much bigger surface than that of the working electrode. Its isolated compartment is a glass tube enclosed in a sheet of sintered glass (porosity 4). The reference electrode described by Barale *et al.* [48], is a silver wire dipped in a eutectic medium saturated with silver sulphate (Fig. 2a). Like most metals, silver is attacked in a molten medium [49]. The overall reaction is:

$$2Ag + 2S_2O_7^{2-} \longrightarrow 2Ag^+ + SO_2 + 3SO_4^{2-}$$

The saturation of the compartment with Ag_2SO_4 keeps the Ag^+ ion concentration very low in conformity with Cutler's recommendation [37]. All potentials are expressed according to the electrode written as follows: $Ag/Ag_2SO_4/SO_4^{2-}$.

The metals used have a 4 N purity and are obtained from Sochibo. The equipment used is a PRT 20-2X Tacussel potentiostat, a Servovit Tacussel pilot, an EPL1 Tacussel or *X–Y* Sefram recorder and a Beckman 3020 electronic millivoltmeter.

3.5. *Operational techniques*

Naphthalene is swept by means of air or nitrogen over the surface of the eutectic liquid which has already been degassed by means of dry nitrogen for 12 h. This sweeping of reactant vapours over the molten mixture surface is necessary for the following reasons [1]:

(i) a better definition of the contact surface;

(ii) a better control of medium temperature and elimination of hot points;

(iii) a correct control of vanadium pentoxide within the whole reactional volume;

(iv) a good reproducibility of electrochemical curves and chromatograms.

This confirms that reaction takes place at the salt

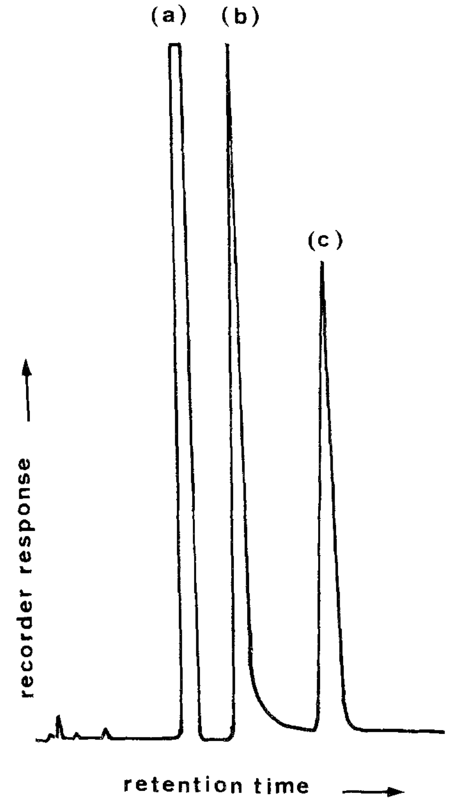

Fig. 3. Vapour phase chromatography analysis of naphthalene oxidation products in eutectic mixture (K_2SO_4–$K_2S_2O_7$) and in the presence of V_2O_5. (a) Naphthalene, (b) phthalic anhydride, (c) 1,4-naphthoquinone.

surface which is continuously renewed by agitation achieved by means of the rotating electrode. A more intense agitation would yield a wavy contact surface, which would lead to an uncertain estimation of its area.

The naphthalene condenser is regulated at a temperature varying from 85 to 100° C which gives naphthalene partial pressures ranging from 9.3×10^{-3} to 18.9×10^{-3} atm.

4. Results

Naphthalene oxidation reactions in the molten eutectic mixture at 425° C and in the presence of V_2O_5 showed that, for a naphthalene flow ranging from 4.5×10^{-6} to 6.7×10^{-6} mol min^{-1} and for V_2O_5 molar fractions varying between 10^{-2} and 5×10^{-2}, the vapour mixture of the organic products contained mainly phthalic anhydride, 1,4-naphthoquinone and unreacted naphthalene. Figure 3 shows a typical chromatogram.

These catalytic reactions are, in fact, double redox reactions in which the solvent can take part. During the surface sweeping of the bath without V_2O_5 by nitrogen carrying naphthalene, sulphur dioxide was formed as shown by the discharge of the iodine solution at the reactor exit and by the current–potential curves (Fig. 4), which are comparable to those recorded during the oxidation of SO_2 to SO_3 [27].

A eutectic bath containing V_2O_5 swept by a gaseous flow of naphthalene (carried by nitrogen) changes colour from reddish brown to green, because of the change from V(V) to V(IV). It is now widely accepted that, in these molten salts, it is the couple V(IV)/V(IV) which is considered [48]. The green solution thus obtained cannot turn reddish brown when swept by atmospheric oxygen; the results being thus identical to those obtained with air on a eutectic bath containing vanadium oxysulphate (IV).

In the light of these three qualitative experiments, our proposal is that the naphthalene oxidation in a K_2SO_4–$K_2S_2O_7$ medium and in the presence of V_2O_5 takes place according to a three-step process which can be summarized as follows:

(i) reduction of the eutectic bath by naphthalene

$$C_{10}H_8 + S_2O_7^{2-} \longrightarrow SO_2 + \text{oxidation products} \qquad (I)$$

(ii) regeneration of the bath (oxidation of dissolved SO_2) by V_2O_5

$$S(IV) + 2V(V) \longrightarrow S(VI) + 2V(IV) \qquad (II)$$

(iii) regeneration of the catalyst by atmospheric oxygen

$$O(0) + 2V(IV) \longrightarrow O(-II) + 2V(V) \qquad (III)$$

5. Interpretations

When studying the oxidation of SO_2 to SO_3 by air in the same medium, Comtat [27] suggested a kinetic equation for step II. Therefore, details will only be given for steps I and III.

5.1. *Kinetics of potassium disulphate reduction by naphthalene*

The rate of step I can be written as:

$$V_1 = \frac{d}{dt}[SO_2] = K_1 P^{1}_{C_{10}H_8}$$

Degeneration of the order with respect to the disulphate ion can be observed due to bath saturation with potassium sulphate, the following equilibrium being taken into account:

$$S_2O_7^{2-}(\text{liq}) \rightleftharpoons SO_4^{2-}(\text{s}) + SO_3(\text{g})$$

The $S_2O_7^{2-}$ concentration can thus be kept constant.

We used two electrochemical methods in order to determine the initial rate of this reduction and evaluate the pseudo-constant K_1 and the partial order α_1 with respect to naphthalene. The first consists of following the variation of the equilibrium potential of the working electrode with time (Fig. 5) during sweeping of the bath with naphthalene carried by nitrogen. In the second, the variation of the limiting current with time is measured (Fig. 6).

5.1.1. Variation of the equilibrium potential as a function of time. The redox equilibrium of the S(VI)/S(IV) couple which comes into play during the reduction of

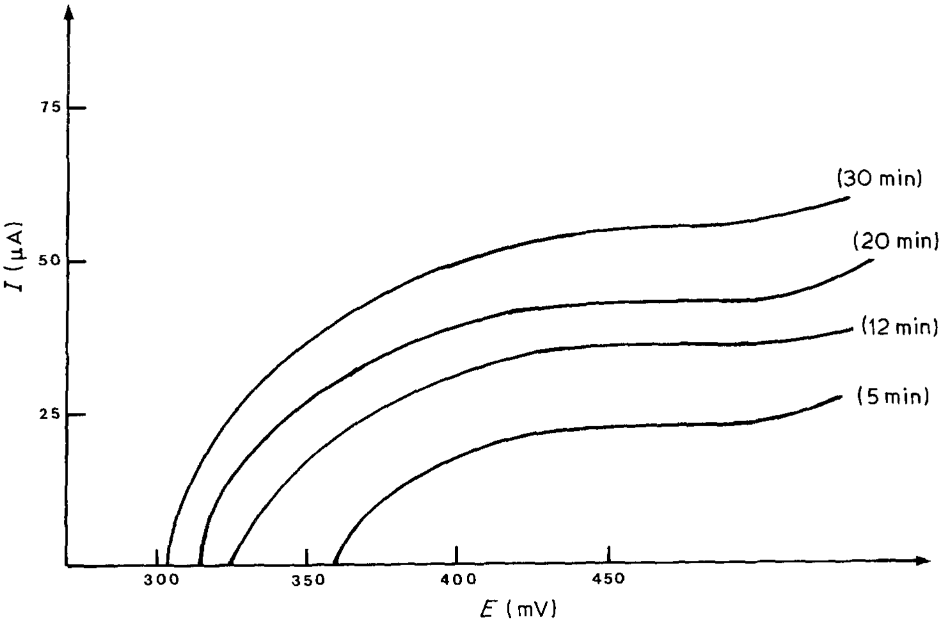

Fig. 4. Current–potential curves at different times of reduction of the eutectic mixture (K_2SO_4–$K_2S_2O_7$) by naphthalene ($P_{C_{10}H_8} = 18.9 \times 10^{-3}$ atm) carried by nitrogen.

potassium disulphate to sulphur dioxide by naphthalene can be expressed as follows:

$$2S_2O_7^{2-} + 2e^- \rightleftharpoons SO_2 + 3SO_4^{2-}$$

The expression of the equilibrium potential of the platinum electrode for this electrochemical reaction is:

$$E = E_S^0 - \frac{RT}{2F} \log_e P_{SO_2} [SO_4^{2-}]^3 \qquad (1)$$

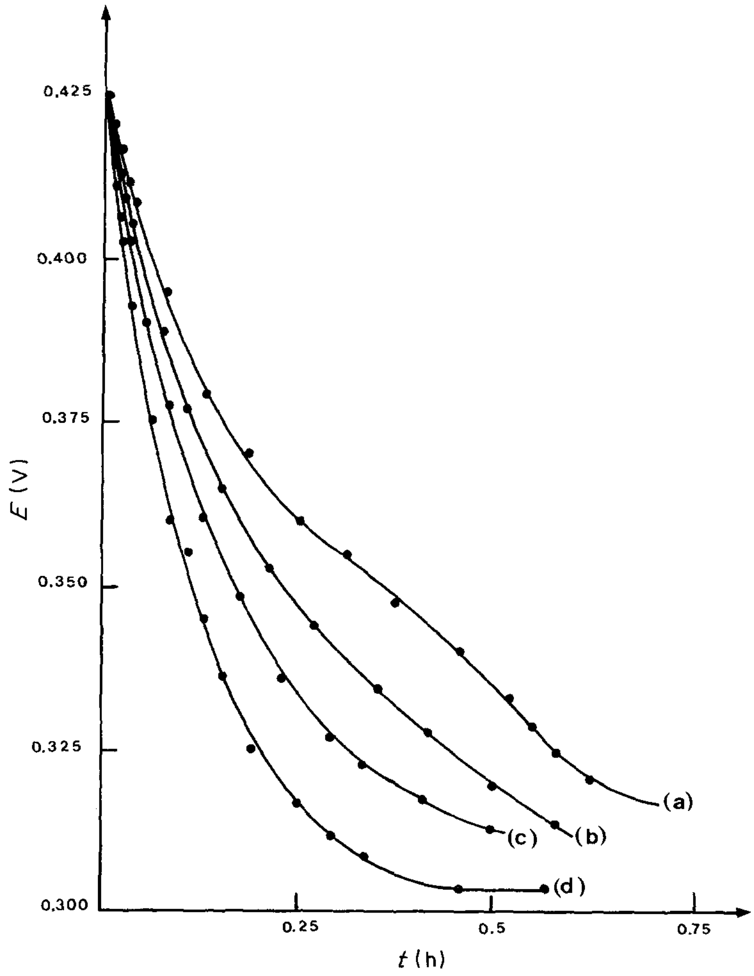

Fig. 5. Equilibrium potential as a function of time for different naphthalene pressures: (a) $P_{C_{10}H_8} = 9.3 \times 10^{-3}$ atm, (b) $P_{C_{10}H_8} = 12.4 \times 10^{-3}$ atm, (c) $P_{C_{10}H_8} = 15.4 \times 10^{-3}$ atm, (d) $P_{C_{10}H_8} = 18.9 \times 10^{-3}$ atm.

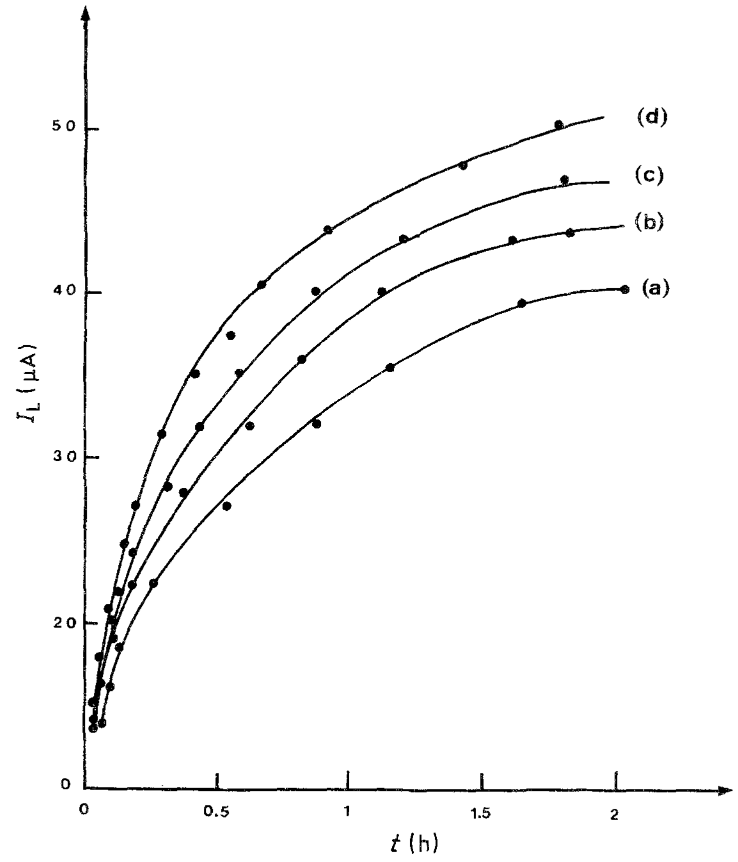

Fig. 6. Limiting current vs time of naphthalene (at different pressures) reaction on K_2SO_4-$K_2S_2O_7$ mixture: (a) $P_{C_{10}H_8} = 9.3 \times 10^{-3}$ atm, (b) $P_{C_{10}H_8} = 12.4 \times 10^{-3}$ atm, (c) $P_{C_{10}H_8} = 15.4 \times 10^{-3}$ atm, (d) $P_{C_{10}H_8} = 18.9 \times 10^{-3}$ atm.

The partial pressure of a gas is related to its concentration by the Henry's law constant. Applied to SO_2:

$$\gamma_{SO_2} = \frac{P_{SO_2}}{[SO_2]} \tag{2}$$

SO_2 concentration is obtained from Equations 1 and 2, and its derivative at initial time gives the expression:

$$\begin{aligned} V_1^0 &= K_1 P_{C_{10}H_8}^{\alpha_1} \\ &= -\frac{2F}{RT}\left\{\exp\frac{2F}{RT}(E_S^0 - E^1) - 3\log_e[SO_4^{2-}]\right. \\ &\quad \left. - \log_e\gamma_{SO_2}\right\}\left(\frac{dE}{dt}\right)_0 \end{aligned} \tag{3}$$

The logarithmic transform of this equation can be written as follows:

$$\log_e\left(-\frac{dE}{dt}\right)_0 = \alpha_1 \log_e P_{C_{10}H_8} + \log_e K_1 + C \tag{4}$$

with

$$\begin{aligned} C &= 3\log_e[SO_4^{2-}] + \log_e\gamma_{SO_2} - \log_e\frac{2F}{RT} \\ &\quad - \frac{2F}{R}(E_S^0 - E^1) = \text{constant} \end{aligned}$$

given the fact that the medium is saturated in SO_4^{2-} and consequently $[SO_4^{2-}]$ = solubility = $C^*_{SO_4^{2-}}$.

$(dE/dt)_0$ experimental values are determined by an estimation of the origin tangent slopes for the curves of equilibrium potential as a function of time (Fig. 5) for different naphthalene partial pressures. The expression of the $\log_e(-dE/dt)_0 = f(\log_e P_{C_{10}H_8})$ straight line determined according to the method of least squares is:

$$\log_e\left(-\frac{dE}{dt}\right)_0 = 1.1\log_e P_{C_{10}H_8} + 4.4$$

with a correlation coefficient 0.966. The kinetic constants are then partial order versus naphthalene $\alpha_1 = 1.1$ and apparent constant $K_1 = 2.2 \times 10^{-2}$ mol dm^{-3} h^{-1} atm^{-1}.

5.1.2. *Variation of the maximum current as a function of time.*

The variation of the sulphur dioxide concentration as a function of time is proportional to the variation of the limiting current observed on the current-potential curves for the electrochemical oxidation of this gas (Fig. 4).

In this case, the initial rate can be written as follows:

$$V_1^0 = \frac{d}{dt}[SO_2] = \frac{1}{K}\left(\frac{di_L}{dt}\right)_0 = K_1 P_{C_{10}H_8}^{\alpha_1} \tag{5}$$

with K_D the proportionality coefficient obtained from the ratio of the limiting current corresponding to saturation of sulphur dioxide solubility in the eutectic mixture [27].

The logarithmic transform of expression 5 gives:

$$\log_e\left(\frac{di_L}{dt}\right)_0 = \alpha_1\log_e P_{C_{10}H_8} + \log_e K_1 K_D \tag{6}$$

$(di_L/dt)_0$ experimental values are determined from the origin tangent slopes of the curves of limiting current versus time (Fig. 6). Determined with the method of least squares and with a 0.993 correlation coefficient, the expression of the straight line according to Equation 6 is:

$$\log_e \left(\frac{di_L}{dt} \right)_0 = 1.0 \log_e P_{C_{10}H_8} + 3.0$$

In this case the kinetic constants are $\alpha_l = 1.0$ and $K_l = 1.9 \times 10^{-2}\,\text{mol dm}^{-3}\,\text{h}^{-1}\,\text{atm}^{-1}$.

Both electrochemical techniques give the same values within 10% for α_l and within 20% for K_l. For the oxidation of naphthalene by the potassium sulphate–disulphate eutectic mixture, the expression of the initial rate is:

$$(V_1^0)_{C_{10}H_8} = 2.1 \times 10^{-2} P_{C_{10}H_8}$$

This expression has to be compared to expressions (translated into the same unit system) for the oxidation rates of 1-butene on the one hand [32] and *o*-xylene [33] on the other hand in the same bath:

$$(V_1^0)_{C_4H_8} = 50.4 \times 10^{-2} P_{C_4H_8}^{1.1}$$

$$(V_1^0)_{o\text{-xyl}} = 3.3 \times 10^{-2} P_{o\text{-xyl}}^{1.1}$$

Therefore it seems that the bath reduction rate is high in the case of 1-butene, but remains comparable for both aromatic hydrocarbons although slightly lower in the case of naphthalene.

5.2. *Kinetics of vanadium(IV) oxidation by gaseous oxygen*

Vanadium oxisulphate is dissolved in a K_2SO_4–$K_2S_2O_7$ eutectic mixture, at the initial 5×10^{-3} mole fraction (m.f.) concentration. Atmospheric oxygen is swept on to the liquid surface with a $100\,\text{cm}^3\,\text{min}^{-1}$ flow. Vanadium(IV) concentration is followed by means of a platinum electrode both by measuring the equilibrium potential and by determining the limiting current from the current–potential curve related to the oxidation, with means that at any given moment, the following expression can be written on the one hand:

$$[V(IV)]_t = \frac{[V(IV)]_0}{1 + \exp \frac{F}{RT}(E - E_v^0)} \tag{7}$$

and on the other hand:

$$(i_L)_t^v = K[V(IV)]_t \tag{8}$$

Figure 7 represents the variation of the inverse mole fraction of vanadium(IV) as a function of time for two partial oxygen pressures. The linearity of this representation over very long periods of time shows that one is dealing with a second order reaction with respect to vanadium(IV) if an order degeneration is supposed to take place *vis-á-vis* the oxygen dissolved in the bath, an assumption which will be confirmed later. Similarly, the comparison between the curves obtained with oxygen on the one hand and air on the other hand shows that the reaction is first order with respect to oxygen partial pressure.

The rate law which can be deduced from these measurements is

$$V_3 = -1 \frac{d[V(IV)]}{dt} = 82.8 P_{O_2} [V(IV)]^2 \tag{9}$$

with P_{O_2} in atm, [V(IV)] in mole fraction (m.f.) and t in h. The concentration of dissolved oxygen must now be shown not to have changed significantly in order to justify the order degeneration previously postulated.

The vanadium(IV) oxidation rate equation can be expressed with reference to the concentration of dissolved oxygen. In fact, the current–potential curves show the exisence of reduction, on the platinum electrode, of oxygen dissolved in the mixture without vanadium.

Given the fact that, on the liquid surface, the gas concentration is equal to the solubility C^*, the gas absorption rate in the liquid can be written as

$$\frac{dC^0}{dt} = K_L a'(C^* - C^0) \tag{10}$$

C^0 = gas concentration, supposed uniform, in the liquid (mol cm^{-3}); K_L = physical coefficient of mass transfer (cm s^{-1}); a' = exchange area per unit of volume (cm^{-1}). In this case, the integration of the differential equation gives

$$K_L a' t = \log_e \frac{C^*}{C^* - C^0}$$

Expression 8 leads to

$$K_L a' t = \log_e \frac{C^*}{C^* - C^0} = \log_e \frac{i_L^*}{i_L^* - i_L} \tag{11}$$

a' can be determined, knowing the volume of the liquid and the contact area presented to the gas. The Henry's law constant applied to oxygen gives the relationship between its partial pressure and its solubility. The expression for the vanadium(IV) oxidation rate can be written as follows:

$$V_3 = -\frac{d[V(IV)]}{dt} = 5.4 \times 10^4 C^0 [V(IV)]^2 \tag{12}$$

The values used in relation to C^*, K_L and γ_{O_2} are given in the nomenclature.

It must now be established that the order degeneration with respect to oxygen is correct. In the presence of vanadium(IV), the material balance carried out on oxygen, taking the absorption and the chemical reaction into account is

$$K_L a'(C^* - C^0) = \frac{dC^0}{dt} + K_3' C^0 [V(IV)]^2 \tag{13}$$

Considering that the oxidation reaction is first order with respect to oxygen, Equation 13 can be written as follows:

$$K_L a'(C^* - C^0) = \frac{dC^0}{dt} + K' C^0 \tag{14}$$

The integration of the differential Equation 14 with $C^0 = 0$ at $t = 0$ leads to

$$C^0 = \frac{K_L a' C^*}{K_3' + K_L a'} \{1 - \exp[-(K_3' + K_L a')t]\}$$

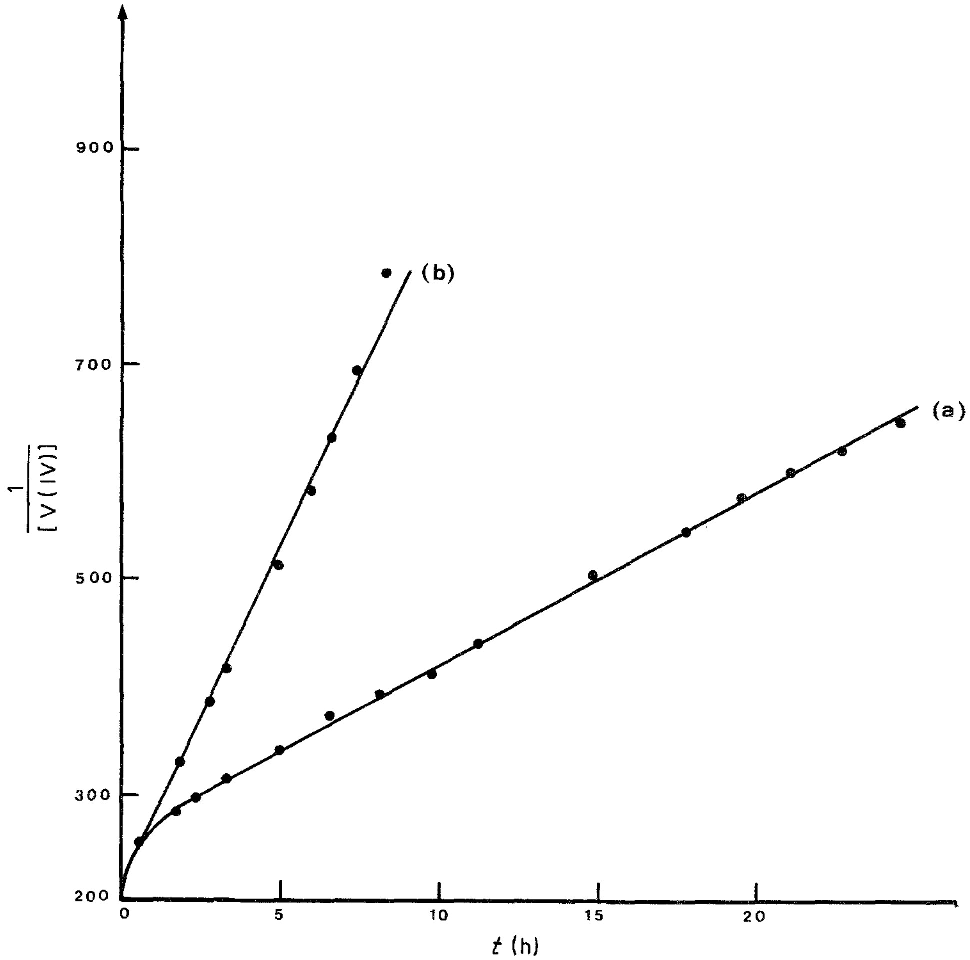

Fig. 7. Inverse of mole fraction of the vanadium(IV) as a function of time for two partial oxygen pressures: (a) P_{O_2} = 0.2 atm, (b) P_{O_2} = 1 atm.

$(K_3' + K_L a')$ equals approximately 1.5, the equilibrium condition $dC^0/dt = 0$ is reached in less than a minute, C^0 equals $3.4 \times 10^{-4} C^*$ and [V(IV)] change during the time needed to obtain this quasi-stationary condition is negligible.

6. Discussion

Initial rates of the three proposed steps, expressed in the same system unit are:

(i) disulphate reduction by naphthalene

$$V_1^0 = 2.1 \times 10^{-2} P_{C_{10}H_8}$$

(ii) bath reoxidation by vanadium(V)

$$V_2^0 = 19.2 \times 10^{-2} P_{SO_2}$$

(iii) catalyst regeneration by oxygen

$$V_3^0 = 82.8 P_{O_2}[V(IV)]^2$$

Given the fact that, for a short reaction time, the vanadium(IV) concentration is very low, the catalyst regeneration step is shown to remain the slowest. On the other hand, the bath reoxidation step is the fastest. Thus, after prolonged use of this catalytic bath, only a few minutes of bubbling atmospheric oxygen is necessary to regenerate the catalyst.

7. Conclusion

Electrochemical study of the catalytic oxidation of naphthalene in molten sulphate pyrosulphate at 425° C with vanadium pentoxide has made it possible to:

(i) present the different steps necessary for the reaction;

(ii) compare their initial rates;

(iii) follow the evolution of the catalysts *in situ*;

(iv) show the important role played by the solvent which differentiates it from that played by catalyst supporter used in gas–solid catalysis;

(v) show that in a molten salt medium, the redox system V(V)/V(IV) allows the regeneration of the solvent, whereas in the solid phase it, in fact, constitutes the catalyst.

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