A THERMOMETRIC STUDY ON THE OXIDATION OF ISOPROPYL ALCOHOL IN SOME MINERAL ACIDS

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ABSTRACT

Isopropyl alcohol is readily oxidized by HNO_3 at room temperature with the evolution of a considerable amount of heat. The reaction is followed by the thermometric technique. The temperature–time curves reveal, after the induction period, that the oxidation reaction proceeds in two consecutive steps, the first to acetone then to acetic and formic acids. It has been found that the reaction is first order with respect to the first step and second order for the latter stage. The activation energy of the reaction is calculated.

Hydrochloric and sulphuric acids do not react with isopropyl alcohol at room temperature except in the presence of an oxidizing agent, e.g. $K_2Cr_2O_7$ or $KMnO_4$. The effect of varying the initial temperature as well as different additives on the thermometric behaviour of the reaction are studied and a mechanism of the reaction is proposed.

INTRODUCTION

The thermometric technique has proved to be an effective and rapid measure for the dissolution of metals [1–6] and alloys [7,8] in a variety of attacking media and for elucidation of corrosion inhibition by surface active agents and additives [1,4,5,7,9–13]. In a recent publication [14], the dissolution of copper, zinc and copper–zinc alloy was studied in nitric acid by the thermometric technique. It was found that this dissolution was influenced by the presence of some alcohols. The degree of dissolution of the tested metals depends on the nature, chemical properties and concentration of the alcohol as well as the acid strength. It was noticed [14] that some of the tested alcohols, e.g. isopropyl alcohol, show a chemical reaction with nitric acid, even in the absence of the metal at room temperature.

It seemed of interest to examine the chemical reaction of isopropyl alcohol and some mineral acids by the thermometric technique. The study aims to throw light on the acid decomposition of the alcohol and the effect of some variables on the stability of the compounds, the order of reaction and thermodynamic parameters. Shams El Din and Arain [15] recently used the thermometric technique to examine the stability of dibutyl thiourea in

acid solutions. They [15] found that the reaction is bimolecular in dibutyl thiourea and of fifth order in HNO_3, and has an activation energy of 14 kcal mol^{-1}.

EXPERIMENTAL

The thermometric reaction vessel and the experimental setup were the same as described elsewhere [4,16]. The total volume of the reaction solution is 15 ml, and unless otherwise stated, the initial temperature was 23°C. The variation of the temperature of the system was measured to ± 0.1°C on a calibrated thermometer. All chemicals were of AR quality and were prepared by recommended procedures. Experiments, carried out under identical conditions, were highly reproducible with a deviation of ± 0.5°C in the maximum temperature (T_m) and ± 1 min in the time taken (t) to reach it. Due to the comparatively low specific gravity of the alcohol, the solutions were poured into it, to assure better mixing. The reaction number RN is defined as

$$RN = (T_m - T_i)/t = T/t(°C \ min^{-1})$$

where T_m and T_i are the maximum and initial temperatures, respectively, and t the time in minutes taken from the start of the experiment to reach T_m.

RESULTS AND DISCUSSION

The curves of Fig. 1 represent the variation of temperature with time of 15 ml 6 N HNO_3 containing increasing concentrations of isopropyl alcohol ranging between 0.1–2 ml (equivalent to 0.087–1.7 M). The initial temperature T_i of this set of experiments is 23°C. The curves obtained are characterized by an induction period which is increased by decreasing the alcohol concentration. Then the temperature rises quickly to attain a maximum T_m value passing via a discontinuity along the rising parts of the curves. This discontinuity is ill-defined at relatively higher concentrations of the alcohol due to the rapid increase in temperature but is clearly distinguished at lower ones. The maximum temperature of the first T_{m1} and second steps T_{m2} are decreased by decreasing the alcohol concentration and the time to reach T_{m1} and T_{m2} increases. At alcohol concentration $C_{alc} \leqslant 0.52$ M (0.6 ml) the thermometric curves do not rise to the second step (stop at the first step). So RN values decrease by decreasing the concentration of alcohol as can be seen from Fig. 2.

Similar sets of experiments to those exhibited in Fig. 1 were conducted at initial temperatures of 15, 17.5, 20, 30 and 35°C. However, the progressive
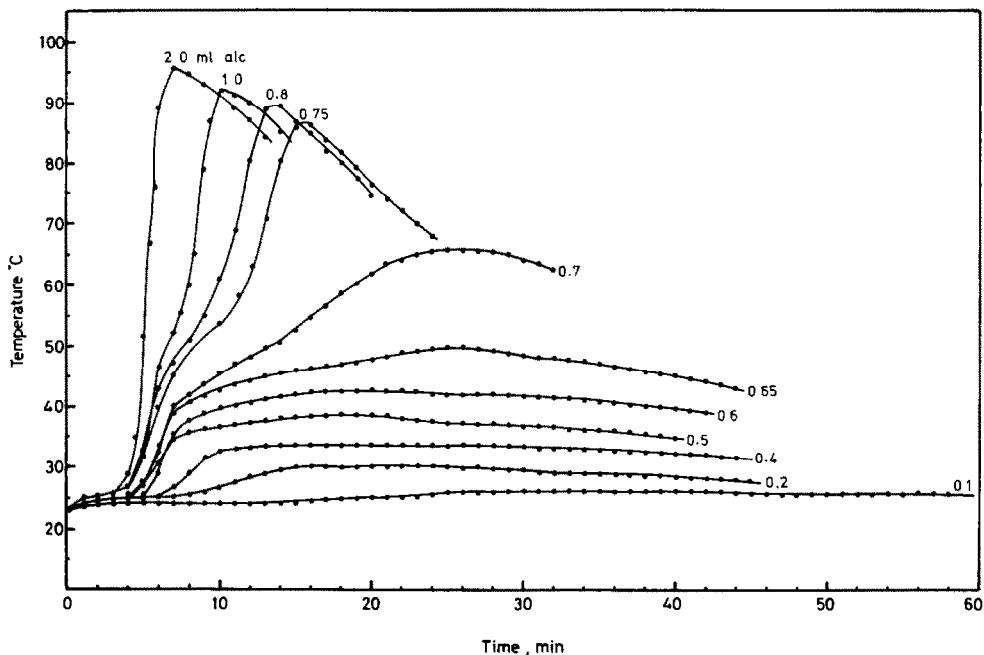
Fig. 1. Variation of temperature with time when adding different amounts of isopropyl alcohol to 6 M HNO_3.

rise of the initial temperature leads to shorter induction periods and much more rapid attainment of maximum temperatures. Therefore higher concentrations of alcohol have to be used when the initial temperature is
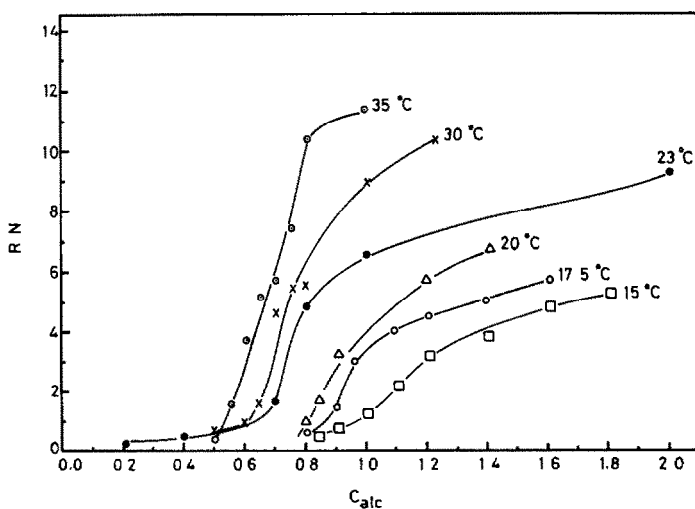

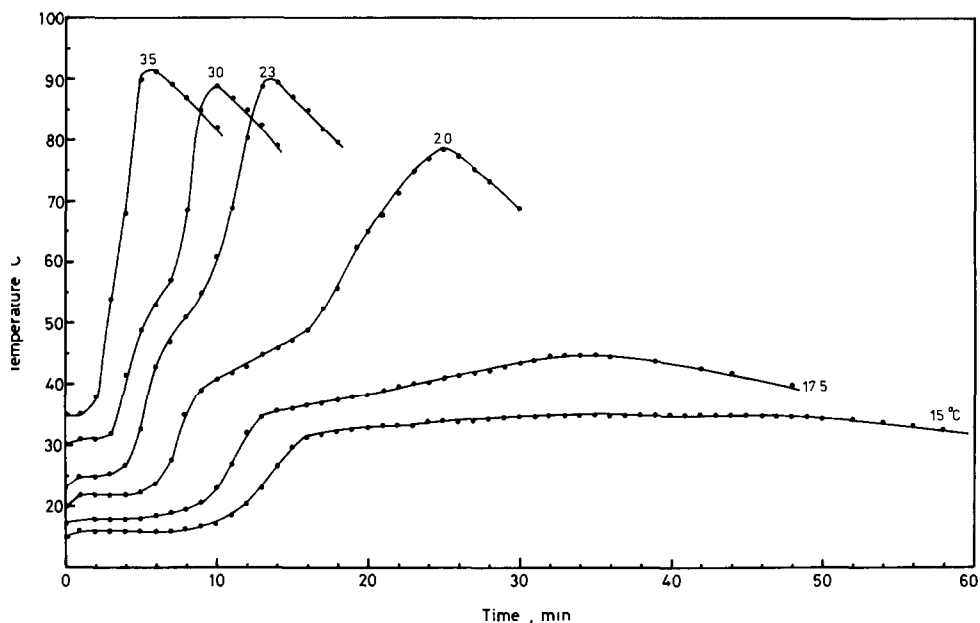Fig. 2. Variation of the RN values with log C_{alc} at different initial temperatures.

Fig. 3. Effect of changing the initial temperature for solutions of 0.696 M (0.8 ml) isopropyl alcohol and 6 M HNO$_3$.

decreased to achieve comparable effects. As an example the effect of changing the initial temperature for solutions of 0.696 M alcohol and 6 M HNO$_3$ is shown in Fig. 3.

The features revealed from Figs. 1 and 3 strongly suggest that the reaction between nitric acid and isopropyl alcohol occurs via three consecutive steps. The first is represented by the induction period, which is the time before the reaction starts and is rate determining. As it is known that nitric acid has powerful oxidizing properties and taking in consideration the tendency of alcohols to be oxidized in acid media, one cannot escape the fact that an oxidation reaction takes place when both are brought into contact.

In solutions of constant acid concentration the rate of reaction, R, between isopropyl alcohol and nitric acid can be expressed in a similar manner to that mentioned by Shams El Din and Arain [15]

$$R = KC_{alc}^n \tag{1}$$

where K is the rate constant, C is the volume of the additive in ml, and n is the order of the reaction with respect to isopropyl alcohol. Further it is considered that at time t of reaching T_m, either for the first or second peak all the alcohol (peak 1) or its intermediate compound (peak 2) have reacted. The average rate R is equal to
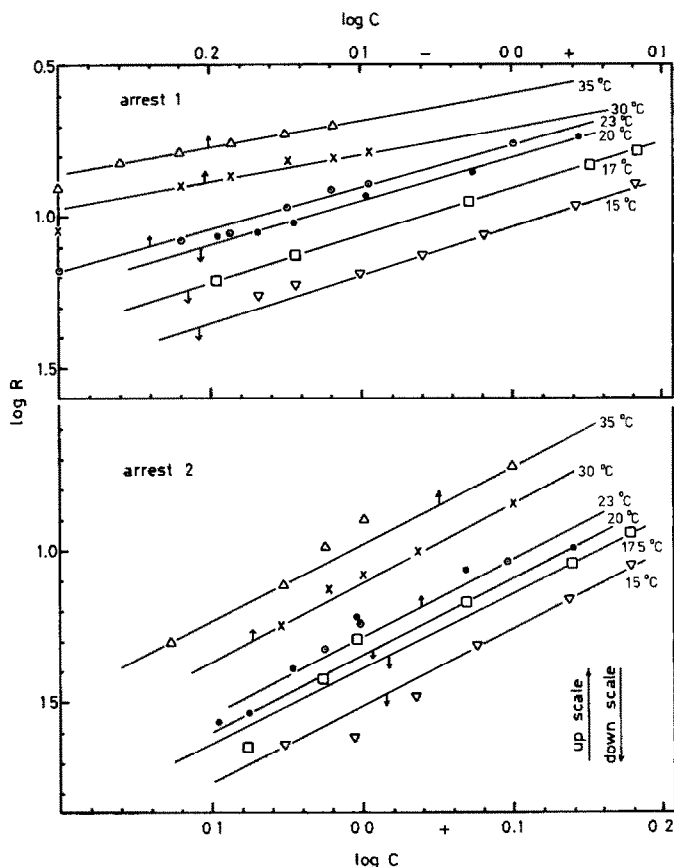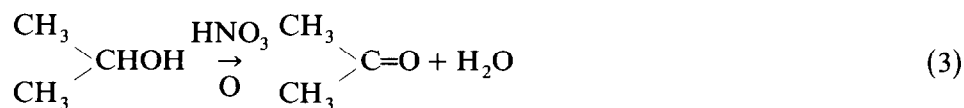
$$R = C/t \tag{2}$$

Fig. 4. Relation between the logarithmic rate of reaction of isopropyl alcohol and nitric acid for the two arrests at different initial temperatures.

According to eqn. (1), at constant temperature the plot of log R versus log C should yield a straight line with a slope equal to n, thus establishing the order of the reaction. The lines intercept the log R axis at the value of log K, enabling the calculation of the specific reaction rate.

Figure 4 exhibits the plots of log R versus log C_{alc} for the reaction of isopropyl alcohol and 6 M HNO_3 for the two peaks at different initial temperatures varying between 15 and 35°C. Invariably straight lines for both cases are obtained which satisfy the general relation (1). The lines obtained are nearly parallel and have slopes ranging from 1.1 to 1.4 for the first step and 2.7–2.8 for the total peak. It can be explained that two consecutive reactions are taking place one after the other. From the results, it seems that the first reaction is first order with respect to alcohol. The second reaction although giving a slope of 2.7, seems to be a second order reaction. The value higher than 2.0 indicates that the first reaction is still occurring and the two reactions are occurring simultaneously. This indicates

that the reaction of isopropyl alcohol with HNO_3 is first order to form the first product (probably acetone) according [17] to

$$\begin{matrix} CH_3 \\ \diagdown \\ CHOH \\ \diagup \\ CH_3 \end{matrix} \xrightarrow[O]{HNO_3} \begin{matrix} CH_3 \\ \diagdown \\ C{=}O + H_2O \\ \diagup \\ CH_3 \end{matrix} \tag{3}$$

Acetone is further oxidized in a second order reaction to a mixture of acetic and formic acids

$$\begin{matrix} CH_3 \\ \diagdown \\ C{=}O \\ \diagup \\ CH_3 \end{matrix} \xrightarrow[O]{HNO_3} CH_3COOH + HCOOH \tag{4}$$

The activation energy of the reaction can be evaluated from the measurements of the rate of reaction at different temperatures. In accordance with the familiar Arrhenius equation

$$R = B \exp(-\Delta H/RT) \tag{5}$$

when plotting log K under similar conditions as a function of the reciprocal of the absolute temperature, straight parallel lines are obtained. Thus the activation energy can be calculated and amounted, according to the experimental conditions, to 6.40 and 12.34 kcal mol^{-1} for the two steps of the reaction.

The reaction between isopropyl alcohol and solutions of HCl or H_2SO_4 of comparable concentrations was too slow to be followed by the thermometric technique. As these acids are equally strong, their slowness in reaction with the alcohol seems to be connected to the experimental conditions as well as the lack of an oxidizing agent as is the case for HNO_3. It could be concluded that the reaction between HNO_3 and isopropyl alcohol is primarily an oxidation reaction. Support to this idea is manifested when adding strong oxidizing agents to solutions of both HCl and H_2SO_4 as shown in Fig. 5. Addition of increments of $K_2Cr_2O_7$ or $KMnO_4$ to the acid solutions causes an instantaneous rise in temperature. The maximum temperature, T_m, varied hand in hand with the oxidant content in the medium. On the other hand, when keeping the oxidant concentration constant, T_m changed proportionally with the acid molarity. The oxidized species of the two oxidants are clearly seen, e.g. amber red colour of the dichromate is changed into the green colour characteristic for the chromic ion, and violet colour of the permanganate is turned turbid by the dioxide formation.

To gain an insight on the nature of the oxidation reaction of isopropyl alcohol with HNO_3, the effects of some additives and acids have been studied. Some features were obtained which can be summarized as follows:

(a) Addition of different concentrations of HCl to 6 M HNO_3 + 2 ml isopropyl alcohol (Fig. 6a) causes a decrease in the induction period and a slight decrease in T_m, so the RN values are increased (acceleration) with C_{HCl} in the medium.
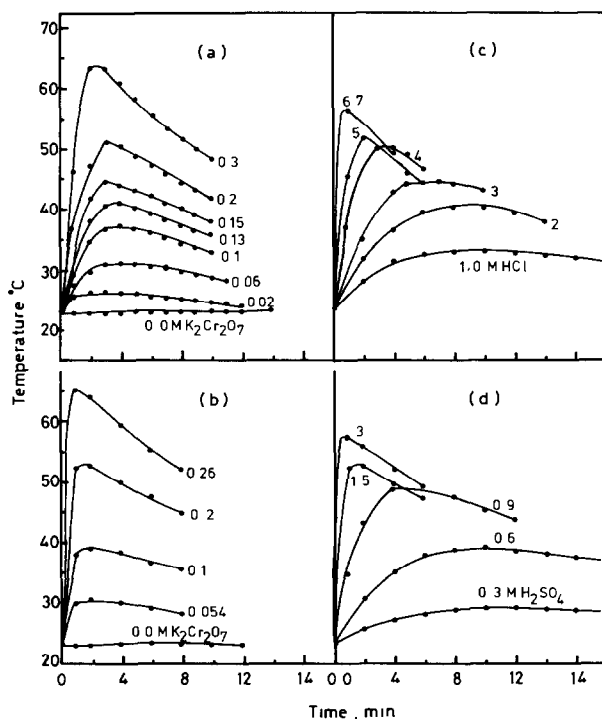
Fig. 5. The thermometric behaviour of: (a) 4 M HCl + 2.5 ml isopropanol + x M $K_2Cr_2O_7$; (b) 1.5 M H_2SO_4 + 2.5 ml isopropanol + x M $K_2Cr_2O_7$; (c) 0.2 M $K_2Cr_2O_7$ + 2.5 ml isopropanol + x M HCl; (d) 0.2 M $K_2Cr_2O_7$ + 2.5 ml isopropanol + x M H_2SO_4.

(b) Change of the ratio of HNO_3 and HCl at constant H^+ concentration, i.e. (HNO_3 + HCl) is always equal to 6 M (Fig. (6b)), causes a decrease in the induction period with a pronounced decrease in T_m. This leads to a pronounced decrease in RN values (inhibition) by increasing HCl content in the solution.

(c) On the other hand, upon addition of KCl, although it produces no effect on the morphology of the curves (Fig. 6c), a pronounced decrease in RN values is noticed. This means that the Cl^- ion has an inhibiting action, while increase of the acid content in the presence of the oxidizing agent can accelerate the reaction depending on the contingent amount of the oxidizing agent.

(d) Addition of sulphuric acid to 6 M HNO_3 accelerates the reaction vigorously, such that at $C_{H_2SO_4} \geqslant 0.5$ M the reaction cannot be followed safely due to the effervesence resulting from the rapid and high increase in temperature.

(e) Increase of H_2SO_4 content in a mixture of H_2SO_4 and HNO_3 at constant $[H^+]$ causes progressive decrease of the induction period and increase in the RN values. At $C_{H_2SO_4} > 2$ M the reaction is too vigorous to be followed.
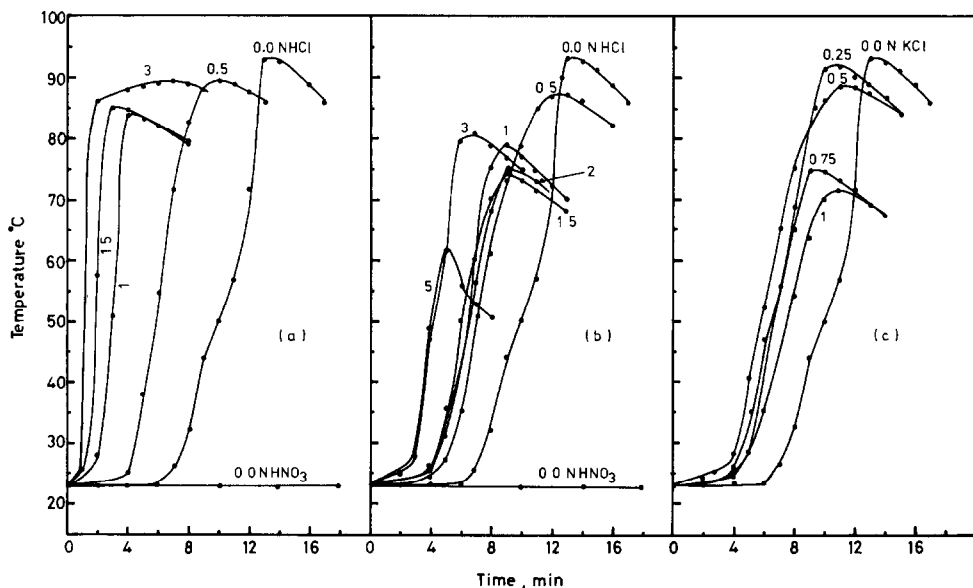
Fig. 6. The effect of: (a) x M HCl + 6 M HNO$_3$ + 2 ml isopropanol; (b) 6 M (HCl + HNO$_3$) + 2 ml isopropanol; (c) x M KCl + 6 M HNO$_3$ + 2 ml isopropanol on the thermometric curves.

(f) The addition of SO_4^{2-} ion to 6 M HNO$_3$ and 2 ml alcohol has no noticeable effect on the morphology or the reaction velocity.

(g) No perceptible influence can be detected for the addition of the NO_3^- ion to 6 M HNO$_3$ + 2 ml isopropanol solution (Fig. 7a). However, the NO_2^- ion exhibits an interesting feature when added to the same solution. The induction period disappears and the temperature rises immediately upon NO_2^- addition to give two well separated steps. The maximum temperature of these steps, T_m, decreases upon increasing the NO_2^- concentration (Fig. 7b). At high concentration of NO_2^- ($\geqslant 0.4$ M) the curve shows only one step. The general outlines of the curves are similar to those obtained when variable isopropanol concentrations are added to 6 M HNO$_3$. Therefore, it seems probable that NO_2^- consumes the alcohol and decreases the amount available to proceed to completion of the reaction in the presence of acid.

The results of the experimental findings allow certain features to be mentioned which shed some light on the mechanism of the oxidation of isopropyl alcohol.

(i) The alcohol reacts vigorously with HNO$_3$ solution upon mixing, with the evolution of considerable amounts of heat. This phenomenon is not noticed when equimolar concentrations of HCl or H$_2$SO$_4$ are mixed with the alcohol.

(ii) The reaction of isopropyl alcohol and HNO$_3$ is primarily an oxidation one, for experiments with HCl or H$_2$SO gave very similar results in the presence of strong oxidizing agents.
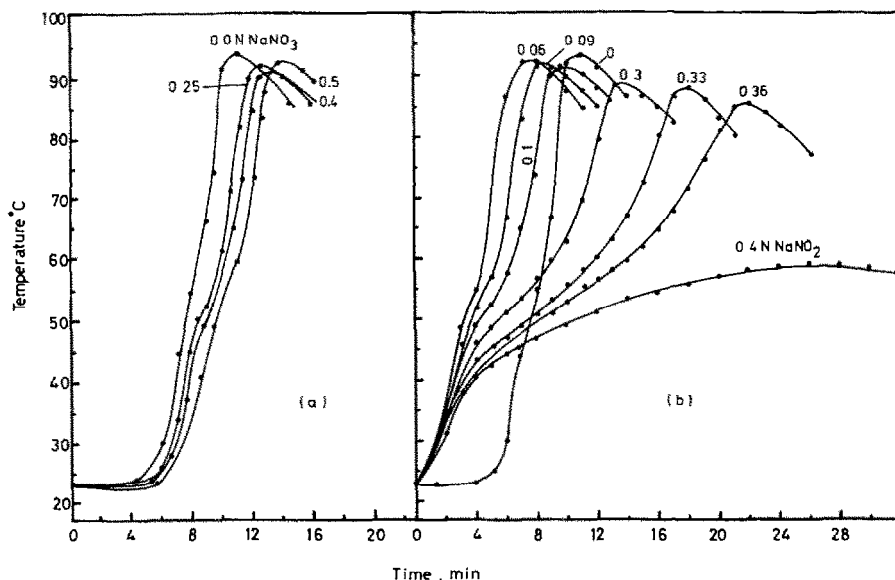
Fig. 7. The effect of addition of: (a) NO_3^-; (b) NO_2^- on the thermometric curves of 6 M HNO_3 and 2 ml isopropyl alcohol.

(iii) The reaction of nitric acid and isopropanol proceeds in two steps: the first is first order while the second is second order.

(iv) The addition of NO_3^- ion to 6 M HNO_3 causes a slight increase of the induction period for the two peaks; however, the maximum temperature remains almost constant. On the other hand the NO_2^- ion nearly obliterates the induction period of the first step and prolongs the time for reaching T_m; the decrease in the T_m also reveals a decrease in the rate of the second reaction.

(v) Neutral chlorides and sulphates produce no effect on the thermometric curves when added to 6 M HNO_3 and 2 ml isopropyl alcohol. When these ions are added in the acid form they cause an acceleration of the reaction due to the increase in acidity.

It therefore seems that the oxidation of isopropyl alcohol in the presence of HNO_3 as an oxidizing agent can be represented by the formation of firstly acetone as mentioned before, according to eqn. (3). Acetone, which is known to be readily oxidized [18,19] even at room temperature, can follow two routes [18]

$$CH_3COCH_3 + 3O \rightarrow CH_3COOH + HCOOH \qquad (6a)$$

$$CH_3COCH_3 + 6O \rightarrow 2HCOOH + H_2CO_3 \qquad (6b)$$
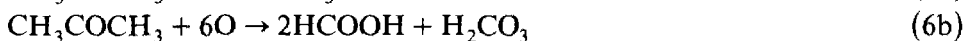
We are in favour of path (6a), as acetone can perform enolisation and the reaction could proceed as

$$CH_3COCH_3 \rightarrow CH_3COCH_2OH \rightarrow CH_3COCHO \rightarrow CH_3COOH + HCOOH$$

$$\qquad (7)$$
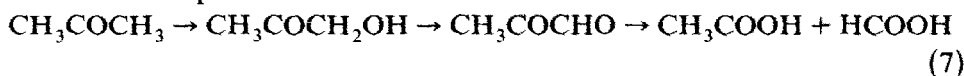
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