JOURNAL OF MATERIALS SCIENCE **24** (1989) 413-419

Evaporation and decomposition of Triton X-100 under various gases and temperatures

KENRO MITSUDA, HIROSHI KIMURA, TOSHIAKI MURAHASHI
Central Research Laboratory, Mitsubishi Electric Corporation, Tsukaguchi-honmachi 8-1-1, Amagasaki-shi, Hyogo, Japan 661

The thermal behaviour of Triton X-100 (surfactant in PTFE dispersion) under various gases was studied with differential scanning calorimetry (DSC) and IR spectrophotometry below 350° C. In nitrogen or argon gas, Triton X-100 evaporated without decomposition. However, in air or oxygen containing gas, thermal oxidation occurred, where a strong ν_{co} band appeared in IR spectra. Oxygen increased the evaporation rate of Triton X-100 remarkably. The heat of vaporization was about 16 kcal mol^{-1} which is independent of the oxygen concentration. The evaporation mechanism is discussed briefly.

1. Introduction

In this paper, the evaporation mechanism of Triton X-100 below 350° C under various gases was studied using a differential scanning calorimeter (DSC) and an infrared spectrophotometer (IR).

Polytetrafluoroethylene (PTFE) is used as a wet-proof and binding agent for a carbon–catalyst mixture in a phosphoric acid fuel cell (PAFC). The polymer can be added as a dispersion of fine particles (0.2 to 0.3 μm diameter) to the carbon–catalyst mixture, where a hydrophilic surfactant is added to stabilize the aqueous dispersion of hydrophobic polymer particles. PTFE dispersion is supplied commonly from Mitsui-fluorochemical (TFE-30J) or Daikin (Polyfuron D-1). Triton X-100 is also used to minimize the particle size of the carbon–catalyst mixture to submicrometre diameters. So Triton X-100 is an important material for fabrication of the PAFC electrode. However it should be removed completely from the electrode, before the operation of the electrode. If it remains it will cause unwelcome influences on the characteristics of the fuel cell. Namely it will produce a worse effect on the wetting properties of the electrode and will cause flooding at the electrode.

Triton X-100 can be removed by leaching the electrode with some organic solvent such as acetone or methanol. However, this method needs much time and care. It can also be removed by thermal decomposition which is of more practical use. In order to decompose it completely a higher temperature is desirable. However, a higher temperature also causes an unwelcome influence on characteristics of PAFC electrode. Namely the damage of carbon (oxidation), sintering of catalyst and strong hydrophobicity can be expected. Thus, it is necessary to select the temperature, atmospheric gas and heat treatment time carefully. For such purpose, it is important to know the thermal behaviour of Triton X-100 under various gases and temperatures.

Holtz *et al.* have reported decomposition of Triton X-100 using DTA–TG technique [1]. They decomposed Triton X-100 absorbed on various carbon powders at higher temperature. They observed exothermic heat during Triton X-100 decomposition. However, their decomposition temperature is still higher than the temperature region of our interest.

We observed also exothermic heat in oxygen containing gases by temperature scanning of DSC measurements. However, temperature scanning of DSC or DTA–TG measurements is unsuitable for our purpose, because the reaction rate is variable. We wish to know how Triton X-100 evaporates or decomposes under various gases at a constant temperature. Thus, isothermal scanning of DSC is preferable. Endothermic heat was observed during isothermal scanning of DSC measurement under various gases. This means that Triton X-100 evaporates or decomposes in our isothermal scanning measurements. DSC is a precise furnace. If the sample weight is measured before and after DSC measurement, evaporation losses of the samples are easily obtained. IR spectroscopy is a useful tool to examine the composition of the sample treated under various experimental conditions. The evaporated deposit in DSC measurement and residue in oven heating are both important samples for IR spectra to consider the evaporation mechanism of Triton X-100.

Thus, our purpose is to clarify the influences of oxygen and temperature on evaporation characteristics of Triton X-100 in the actual temperature region of PAFC electrode fabrication.

2. Experimental details

Triton X-100 was reagent grade (Nakarai Chemicals Ltd). The structural formula of Triton X-100 is given in Fig. 1 [2]. Triton X-100 is a non-ionic surface-active agent which is liquid at room temperature. It is a water-soluble isooctyl phenoxy polyethoxy ethanol [3]. The number of the polyoxyethylene chain is between 9 and 10, which forms a hydrophilic group [2].

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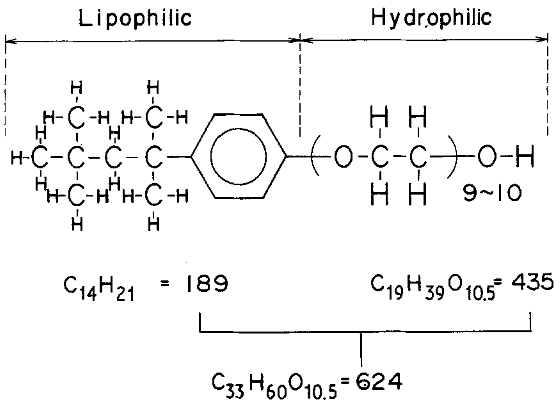

Figure 1 Structural formula of Triton X-100.

The differential scanning calorimeter used was a Perkin-Elmer DSC-2. In isothermal scanning, the heating and cooling rates of the sample were $320\,\mathrm{K\,min^{-1}}$ which will have little influence on the sample. The sample was kept for 30 min at each temperature. Argon, O_2 4.8%–N_2 95.2%, O_2 10%–N_2 90% and air were used as atmospheric gases. The initial sample weight is normally about 3 mg, but in the case of rapid evaporation (within 30 min) the weight ranges between 10 and 20 mg. The sample was loaded in the aluminium sample pan which is 6.5 mm in diameter and 1.5 mm deep. In temperature scanning, the heating rate was $20\,\mathrm{K\,min^{-1}}$ which is sufficient for our purpose. The initial sample weight was below 1 mg in this case. The evaporated deposit of Triton X-100 from the aluminium sample pan was obtained from an upper cover above the sample holder of DSC, because the sample holder cover has two small holes to escape vaporized Triton X-100.

The electric oven (DK-21, Yamato Science Co.) kept the temperature within 5° C with a PID controller (Chino Works Ltd). Sample weight change in the oven was the average value for three samples measured at the same time, using a Sartorius balance (1602 MP) to 0.1 mg order.

IR spectra of the samples were taken with an IR spectrophotometer (Shimadzu IR27G). KRS-5 plate or silicon wafer was used as an IR window for evaporated deposit or residue of Triton X-100.

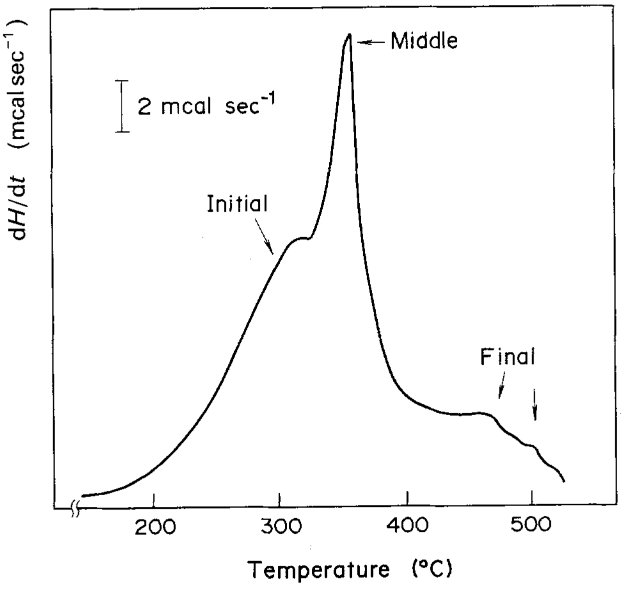

Figure 2 Exothermic curve of Triton X-100 by DSC in air.

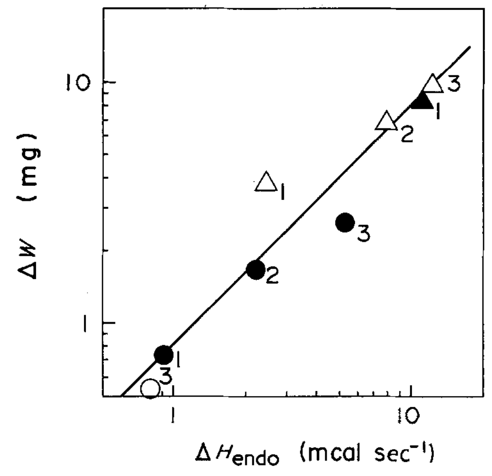

Figure 3 Relationship between evaporated amounts and endothermic heat. (○) 200° C, (●) 250° C, (△) 300° C, (▲) 350° C; 1, O_2 4.8%; 2, O_2 10%; 3, air.

3. Results

3.1. DSC measurement

In this section, the thermal behaviour of Triton X-100 under various gases (different oxygen concentration) between 200 and 350° C is described.

In usual temperature scanning, exothermic heat (2580 to $2700\,\mathrm{cal\,g^{-1}}$) was observed in oxygen 4.8% gas and air, because of thermal oxidation, as Holtz *et al.* obtained in their DTA–TG measurement. However, endothermic heat ($690\,\mathrm{cal\,g^{-1}}$) was observed in argon. A thermogram of DSC measurement in air is shown in Fig. 2. Roughly speaking, Triton X-100 can be oxidized by three steps. The initial step succeeds in the middle step. However the final step is isolated from the other two steps, which is probably due to residual carbon. On the other hand, endothermic heat was always observed in isothermal scanning.

Fig. 3 shows evaporated amounts of Triton X-100 ΔW(mg) plotted against endothermic heat ΔH_{endo} ($\mathrm{mcal\,sec^{-1}}$) obtained with DSC after 30 min heating in oxygen containing gases. Here, ΔH_{endo} was obtained from shifting of the base line. The data of various gases and temperatures are plotted in this figure and yet all of them fit in a straight line. Namely, ΔW are proportional to ΔH_{endo} values. In argon, no appreciable ΔH_{endo} was observed because of smaller weight loss.

Fig. 4 shows evaporated amounts of Triton X-100 ΔW(mg) plotted against reciprocal temperature $1/T$. The straight line holds for each case. As the temperature increases, the weight loss of the sample increases. As the oxygen concentration in the gas increases, the weight loss of the sample increases, which means the oxygen increases the apparent vapour pressure of Triton X-100. Fig. 4 shows the $\log \Delta W$–$1/T$ type relation which resembles the usual vapour pressure data expressed as $\log P = -A/T + B$. The heat of vaporization of Triton X-100 was obtained as $15.7 \pm 0.3\,\mathrm{kcal\,mol^{-1}}$ for four kinds of the gases, which can be defined as

$$\log \Delta W = -\Delta H_{\mathrm{vap}}/RT + \text{constant} \qquad (1)$$

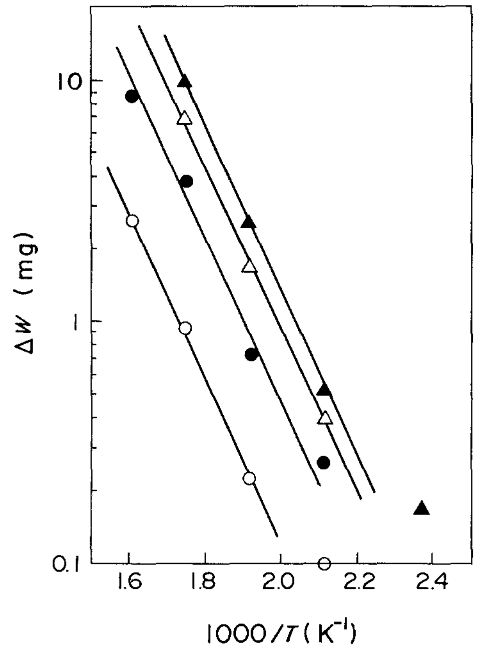

Figure 4 Temperature dependence of evaporated amounts with various gases. (○) Ar, (●) O_2 4.8%, (△) O_2 10%, (▲) air.

The value of ΔH_{vap} is independent of oxygen concentration in the gas.

Fig. 5 shows the evaporated amounts of Triton X-100 W(mg) plotted against oxygen concentration in the gas, $[O_2]$. For each case the straight line holds and the relation is given by

$$\Delta W = A[O_2] + \text{constant} \qquad (2)$$

where A is a constant of proportionality. The effect of oxygen gives a first-order equation such as Equation 2, while temperature gives an exponential term of an Arrhenius plot. From Fig. 5, the ratio of $\Delta W/[O_2]$ (mg/%) can be obtained from each slope. The ratio of $\Delta W/[O_2]$ against $1/T$ is given in Fig. 6. From Fig. 6

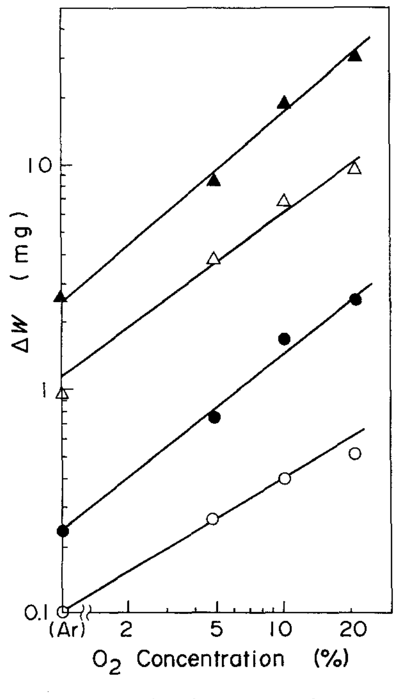

Figure 5 Oxygen concentration dependence of evaporated amounts with various temperatures. (○) 200° C, (●) 250° C, (△) 300° C, (▲) 350° C.

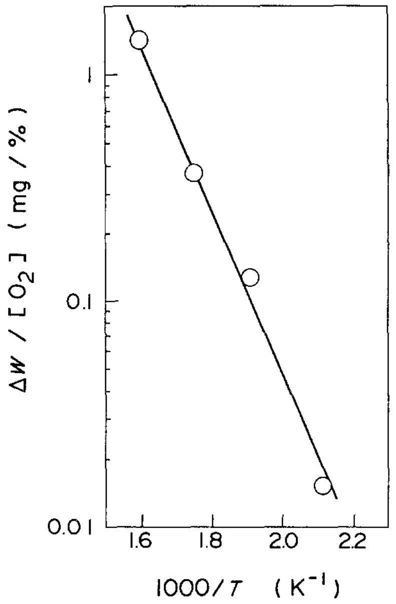

Figure 6 Temperature dependence of evaporated amounts with O_2 concentration.

one obtains the following equation

$$\log(\Delta W/[O_2]) = -\Delta H_{vap'}/RT + \text{constant} \qquad (3)$$

where $\Delta H_{vap'}$ is another heat of vaporization concerned with the influence of oxygen on vapour pressure of Triton X-100. $\Delta H_{vap'}$ was obtained as 16.8 kcal mol^{-1} which agrees with the former value 15.7 within 10%. The influence of oxygen concentration on ΔW increases at higher temperature. Namely at 350° C the ratio is 85 times as large as the ratio at 200° C. These results suggest that Triton X-100 can be evaporated more vigorously by oxygen gas as shown in Fig. 4.

To summarize, three facts were clarified with DSC measurements.

(1) Triton X-100 requires endothermic heat to evaporate.

(2) Evaporation rate increases as the oxygen content of atmospheric gas increases or temperature increases.

(3) The heat of vaporization ΔH_{vap} is independent of the oxygen content in the gas.

3.2. The evaporation of Triton X-100 in an oven

The evaporation of Triton X-100 on silicon wafer was studied under nitrogen gas or air.

Fig. 7 shows the residue of Triton X-100 under nitrogen gas or air after 30 min heat treatment. In air, the residue decreased sharply between 150 and 200° C, while a gradual decrease was observed in nitrogen gas in the same temperature range. However, it is worth noting that the residue decreases slowly in air between 200 and 300° C as a tailend. Namely the evaporation characteristics of Triton X-100 in air differ remarkably from those in nitrogen gas. Nitrogen gas requires a higher temperature for complete evaporation of Triton X-100. However at 350° C the residue is nearly zero either in nitrogen gas or in air.

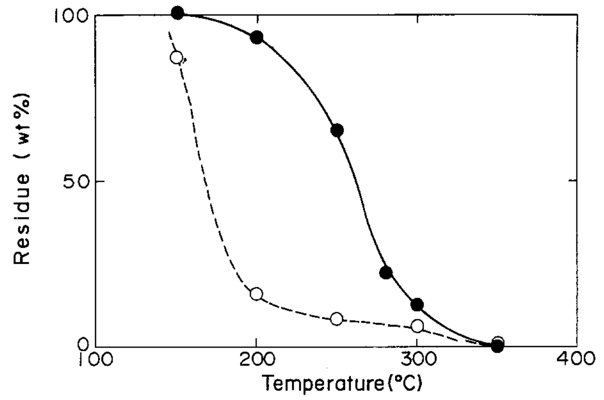

Figure 7 Variation of residue with temperature in active and inactive gases. (○) air, (●) nitrogen.

Fig. 8 shows the detailed evaporation characteristics of Triton X-100 under nitrogen gas between 280 and 360° C for various heating periods. This is a reaction history curve (plot of residue (wt %), 100-X, against time) [4]. A sharp decrease occurs between 300 and 320° C. The curve is sigmoidal (with induction time) below the critical temperature but normal above this temperature [4]. The critical temperature lies between 300 and 320° C, that is, it is about 310° C. Above 310° C Triton X-100 evaporates easily without the tailend.

The detailed evaporation characteristics of Triton X-100 under air between 180 and 300° C are shown in Fig. 9. A sharp decrease occurs between 220 and 240° C. The above transition point is about 230° C. A longer tailend after a sharp decrease of the residue is an inherent characteristic of air treatment. Though considerable evaporation starts at lower temperature compared with that of the nitrogen case, higher temperature is necessary for completion.

To summarize the results, three points can be made.

(1) Triton X-100 evaporates at lower temperatures (50 to 100° C lower) in air than in nitrogen.

(2) In air, a slowly decomposing residue remains, which is a remarkable character of air heat treatment.

(3) Above 310° C Triton X-100 can disappear within 30 min in both nitrogen gas and air.

3.3. IR measurements

The IR spectra of both samples, evaporated deposit and residue, are described to show the evaporation mechanism of Triton X-100 under nitrogen gas or air.

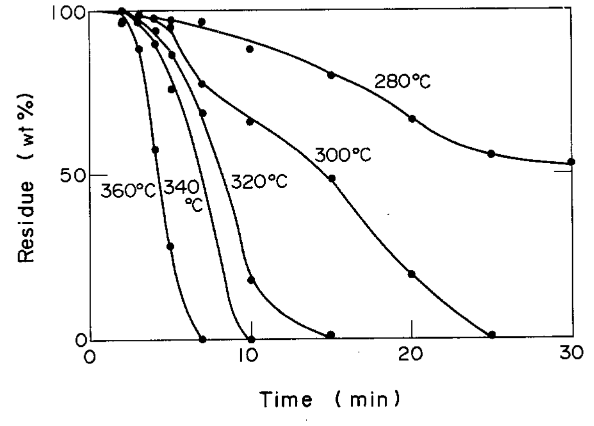

Figure 8 Time dependence of residue in nitrogen.

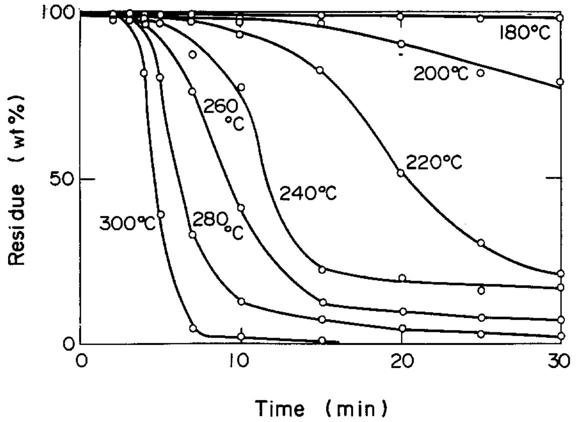

Figure 9 Time dependence of residue in air.

Fig. 10 shows the IR spectra of the residual sample in a nitrogen oven for 30 min at various temperatures. There is no significant change in IR spectra, though gradual weakening of each absorption band was observed at higher temperatures. From these results, it seems that the evaporation mechanism of Triton X-100 under nitrogen gas is a simple evaporation involving no decomposition of the molecules.

The IR spectra of the residue in the air oven for 30 min at various temperatures are given in Fig. 11. A new strong absorption band (1700 cm^{-1}) which is assigned to ν_{co} appeared at 200° C heating. This change is due to oxygen in air, which oxidized molecules in the hydrophilic group. At 300° C, compared with the case of nitrogen, there is no distinguishable Triton X-100 absorption bands in this case. These results in air suggest that the evaporation mechanism of Triton X-100 involves decomposition of the molecules.

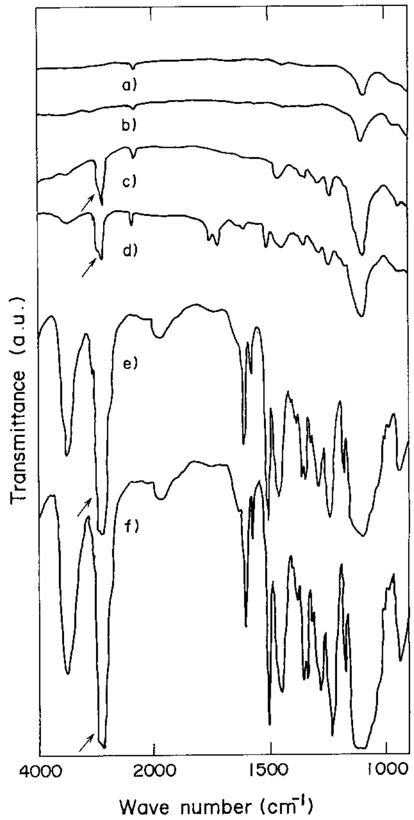

Figure 10 IR spectra of residue in nitrogen. (a) Base line (silicon wafer), (b) 350° C, (c) 300° C, (d) 280° C, (e) 250° C, (f) 150° C.

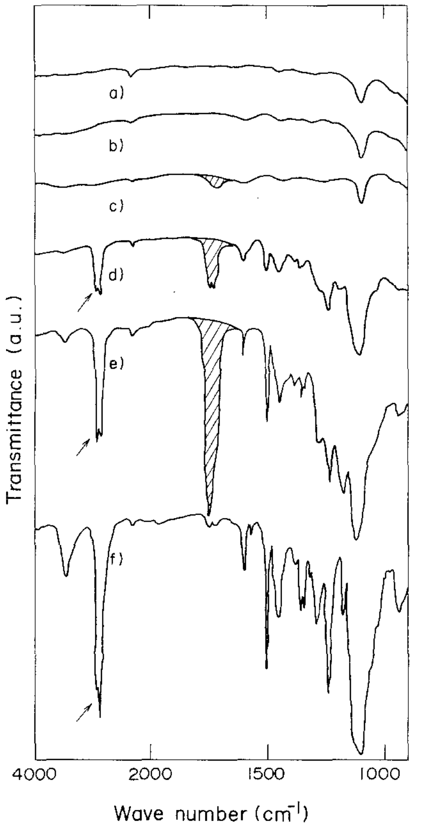

Figure 11 IR spectra of residue in air. (a) Base line (silicon wafer), (b) 350° C, (c) 300° C, (d) 250° C, (e) 200° C, (f) 150° C.

Fig. 12 shows IR spectra of the evaporated deposit in DSC measurements. In argon, there is no significant change in IR spectra compared with the original IR spectra of Triton X-100 or Fig. 10. This fact suggests that simple evaporation occurs in argon with no appreciable decomposition of the molecule. On the other hand, evidence of the thermal decomposition, a new strong absorption band (1700 cm^{-1}) appeared in oxygen 4.8% gas, which was ν_{co}. The spectra resembles that observed at 200° C heating in air oven shown in Fig. 11. Namely, the evaporated deposit of Triton X-100 treated in oxygen containing gas has nearly the same IR spectra as that of the residue of Triton X-100 observed in air oven. Oxygen attacks the molecule in the hydrophilic group, oxidizes it, and changes the evaporation rate and residual fraction.

Applying the base line method to IR spectra [5], the relative absorbance of the ν_{co} band which is a reaction product by oxidation was obtained. The absorbance of the band (2945 cm^{-1}) was standardized as 100%. The results are shown in Fig. 13 as an Arrhenius plot. The following relation is obtained from Fig. 13

$$\log(\nu_{co}) = -\Delta H_{ox}/RT + \text{constant} \qquad (4)$$

where ΔH_{ox} is the activation energy and was calculated as 11.7 kcal mol^{-1}. ΔH_{ox} is considered to be the energy of formation of the ν_{co} band in hydrophilic group of Triton X-100.

To summarize, the following results are obtained.

(1) Triton X-100 evaporates in nitrogen gas without distinguishable decomposition.

(2) Triton X-100 evaporates as partially decomposed form in air, because the hydrophilic groups are oxidized easily by oxygen gas.

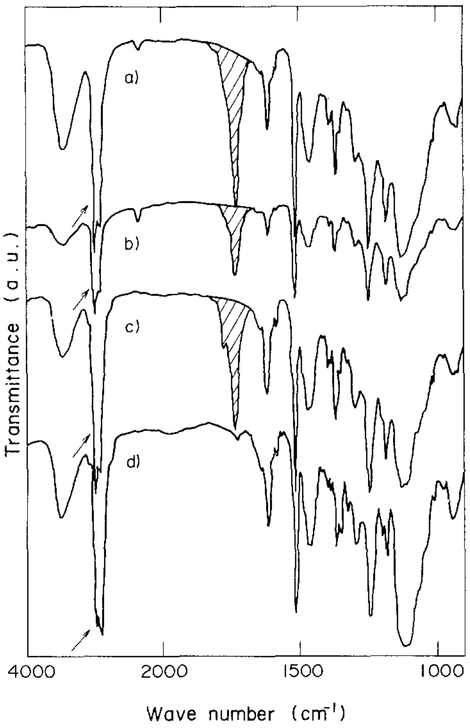

Figure 12 IR spectra of evaporated deposit. (a) Air, (b) O_2 10%, (c) O_2 4.8%, (d) argon.

(3) The evaporated deposit has similar structure to that of the residue, both in nitrogen and in air.

4. Discussion

4.1. The evaporation mechanism of Triton X-100

First we discuss the case of inactive gas. In the IR measurements, the residue spectra (Fig. 10) and the evaporated deposit one (Fig. 12) were similar to the original spectra of Triton X-100. These results are evidence of slight decomposition of the molecule during evaporation.

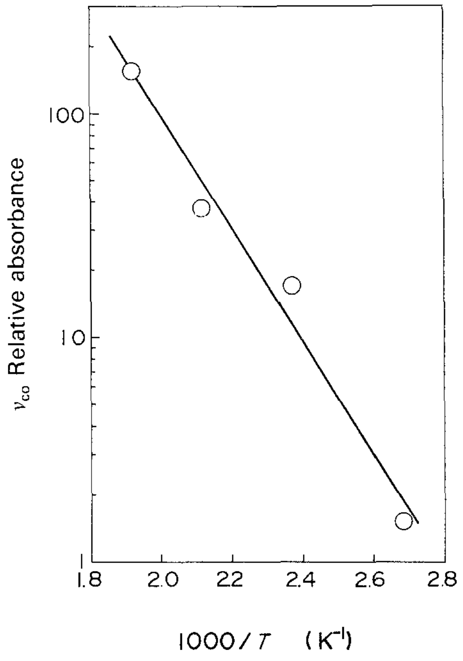

Figure 13 Formation rate of ν_{co} band in Triton X-100 in air plotted against temperature.

Next, the case of oxygen containing gas is discussed. The IR spectra were full of variety as compared with the case of nitrogen or argon. The spectra change was observed both in the residue (Fig. 11) and in the evaporated deposit (Fig. 12). The most remarkable change was the appearance of a new strong absorption band in the 1700 to 1800 cm^{-1} region which was identified as ν_{co} ($C=O$ stretching band) with reference to IR spectra of the other compounds [6]. A close look at the structural formula of Triton X-100 suggests that the easily oxidizable part is the C–O–C bond of polyoxyethylene chain in the hydrophilic group. It can be probably oxidized to –COOH (calboxyl group) which has a CO double bond. This change corresponds to the initial and the middle steps of oxidation shown in Fig. 2.

In addition, there were some changes in the IR spectra. For instance, the absorption band identified as OH stretching at 3500 cm^{-1} region in nitrogen or argon (Figs 10f, 12d) shifted its position to 3450 cm^{-1} in air (Figs 11e, 12a, b and c). This change, that is, weakening of the hydrogen bond, suggests structural change around hydroxyl group (–OH), for example from $-CH_2OH$ to –COOH. Moreover, the absorption and intensity of CH_3- methyl group exceeded that of the $CH_2 =$ methylene group in oxygen containing gas. The methyl group exists only in the hydrophilic group and methylene group exists mainly in the lipophilic group as is shown in Fig. 1. The weakening of the absorption band of the methylene group in oxygen containing gas suggests that the number of the methylene group decreases, namely the polyoxyethylene chain becomes shorter.

Contrary to this, the absorption bands in the 1000 to 1200 cm^{-1} region which were identified as a benzene ring, were unchanged by the presence of oxygen. So we suspected that the lipophilic group is not attacked by oxygen. This may be a source material of final oxidation step in the DSC curve shown in Fig. 2.

The oxidation of Triton X-100 by oxygen is restricted within the hydrophilic group below 350° C. The weight loss data in oxygen containing gas (Figs 7 and 9) clearly show tailend remains which are hard to evaporate. If all of the hydrophilic group is decomposed, and vanishes, only the lipophilic group remains with slower decomposition, reducing the molecular weight from 624 to 189. The weight of the residue is reduced to about one third. The fact that the lipophilic group is apt to remain accounts for the existence of the tailend. However the residue has no surfactant effect at all. From the DSC measurements the heat of vaporization of Triton X-100 is obtained as $15.7 \pm 0.3\,\text{kcal}\,\text{mol}^{-1}$. This value resembles that of some compounds such as octadecan ($\Delta H_{\text{vap}} = 14.5\,\text{kcal}\,\text{mol}^{-1}$), benzyl alcohol ($\Delta H_{\text{vap}} = 12.8\,\text{kcal}\,\text{mol}^{-1}$) [7].

Finally, we compare our results with those of Holtz *et al.* They studied the thermal decomposition of Triton X-100 absorbed on various carbon powders by the TG–DTA technique.

We think it is very difficult to see the effect of oxygen on the thermal behaviour of Triton X-100 absorbed on carbon. Carbon can be oxidized in oxygen containing gas in the 300 to 400° C region with generation of heat and a reduction in its weight. We obtained these results in another experiment. Thus it is difficult to distinguish the reduced weight of Triton X-100 from that of carbon. The DTA–TG technique is less sensible compared with DSC.

4.2. The feasibility of the remains of Triton X-100 in fuel cell electrodes

The effect of oxygen on evaporation of Triton X-100 is by first-order equation as Equation 2. However, temperature effect is that of an exponential term of an Arrhenius plot. Consequently, temperature is superior to oxygen in removing Triton X-100.

The heat treatment of most fuel cell electrodes is done in air [8]. Therefore it is expected that the lipophilic group of Triton X-100 remains after the decomposition of hydrophilic group as is shown by this study. Nevertheless the remains are only the lipophilic group, suggesting the remains have no surfactant effect. However, it is obscure whether or not the remains such as residual carbon produce a harmful effect on the hydrophobicity of the fuel cell electrode.

It is clear that such heat treatment is desirable in the inactive gas and at a temperature as high as possible in order to evaporate Triton X-100 without leaving any trace.

We also used Triton X-100 for fabricating the PAFC electrodes [9]. Moreover our electrodes maintained stability in performance as PAFC during a continuous load for more than 5000 h. The decrease of performance attributable to the flooding of the catalyst layer was not observed.

If the evaporation mechanism of Triton X-100 in the fuel cell electrode resembles the results of this study, one can remove it completely from the fuel cell electrode whether in air or in nitrogen, in the case at 350° C or so and long time (above 30 min) heat treatment.

Consequently we can suppose that the feasibility of the remains of Triton X-100 in fuel cell electrodes is no worry in practice.

5. Conclusions

(1) In an inactive gas, Triton X-100 evaporated with slight decomposition. Vigorous evaporation occurred above 310° C without any trace hard to evaporate.

(2) In an oxygen containing gas, Triton X-100 was oxidized thermally above 230° C, leaving slowly decomposing material.

(3) Oxygen and temperature increased the evaporation rate of Triton X-100 remarkably by a first-order equation, as the exponential term of Arrhenius plot, respectively.

(4) Triton X-100 showed a heat of vaporization of about 16 $\text{kcal}\,\text{mol}^{-1}$, independent of the oxygen content in the gas.

Acknowledgements

This work was supported by Agency of Industrial Science and Technology, Ministry of International Trade and Industry, and New Energy Development Organization (NEDO), Japan.

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Received 28 December 1987
and accepted 6 May 1988