Chapter 5

REACTION KINETICS OF DBDS UNDER THERMAL AGEING

5.1 INTRODUCTION

DBDS is one of the popular and extensively used sulphur compounds which have gained maximum attention in recent years amongst hundreds of sulphur species. This compound is also used in mineral transformer oil which is primarily a coolant as well as an insulant for the power apparatus. In case of transformers which operate at high voltages and very high electrical and thermal stresses, the reaction of DBDS on copper conductors over a range of temperature have led to the formation of copper sulphide (Cu$_2$S) and starts migrating towards inner paper layers to cause thermal imbalance in the insulation system and electric field distortion. It finally leads to breakdown of insulation and failure of transformers.

In this background, the mechanism of formation of copper sulphide in transformers has extensively studied throughout the world [1-4]. Because of the complexities involved, it has been difficult to come to definite conclusion about the degradation of DBDS in mineral insulating oil. It is interesting to observe that DBDS is introduced into the transformer either intentionally or even accidentally and because of its good and natural property as an antioxidant [5], it is expected to improve the oxidation stability of mineral oil. Since DBDS enhances the lubricating capacity of the oil, it has been extensively used in many industrial applications and hence a large data is available highlighting its mechanism of tribo-chemical reactions [6-7]. However, reactions of DBDS in high
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Voltage Power apparatus are more complex than what is fairly well understood in mechanical applications since temperature variations could be high from 100 to 150°C and there are chances of occurrences of hot spots which will be at much higher temperatures. Therefore different approaches for understanding the degradation mechanisms of DBDS are inevitable in case of Power apparatus. The understanding of the mechanism involved in degradation of DBDS is further complicated by the variations in its reaction with copper leading to formation of copper sulphide.

Many different reaction mechanisms are reported in literature, describing the degradation of DBDS in mineral insulating oils. According to Lance Lewand [8], DBDS in oil cleaves into benzyl mercaptan which is highly reactive towards copper. The reaction of benzyl mercaptan with copper leads to the formation of copper sulphide along with ethyl benzene as shown in equations (5.1) and (5.2) [8].

\[
\Delta (C_6H_5CH_2)_2S_2 \rightarrow 2C_6H_5CH_2SH \tag{5.1}
\]

\[
2C_6H_5CH_2SH + 4Cu^+ \Delta \rightarrow 2Cu_2S + 2C_6H_5CH_2CH_3 \tag{5.2}
\]

Some authors [9] have reported a slightly different approach involving radicals leading to the formation of copper sulphide. According to the authors [9], DBDS reacts with copper forming a complex. This DBDS-Copper complex decomposes leading to the formation of copper sulphide and other by-products as shown in equation (5.3) and (5.4).

\[
2Cu(S) + (C_6H_6CH_2)_2S_2 \text{ (in oil)} \rightarrow (C_6H_6CH_2)_2S_2 - Cu_2(S) \rightarrow Cu_2S(S) + C_6H_6CH_2^* \text{ (in oil)} + C_6H_6CH_2S^* \tag{5.3}
\]

\[
C_6H_5CH_2^* \text{ (in oil)} + C_6H_6CH_2S^* \text{ (in oil)} \rightarrow \frac{1}{4} C_6H_5CH_2CH_2C_6H_6 \text{ (in oil)[Bibenzyl - BiBz]} + \frac{1}{2} (C_6H_5CH_2)_2S \text{ (in oil)[dibenzyl sulphide]} + \frac{1}{4} (C_6H_5CH_2)_2S_2 \text{ (in oil)[DBDS]} \tag{5.4}
\]

Researchers have also concentrated on the study of kinetics of the reaction of DBDS with copper conductors in transformer oil [10]. The authors have observed that the formation of copper sulphide is a function of concentration of DBDS and temperature of oil.

The rate of a reaction is defined as change in concentration with time; \( \frac{d[DBDS]}{dt} \); where \([DBDS]\) is the concentration of DBDS. The rate equation relates the reaction rate
with concentrations of the reactants by a rate constant. The order of a reaction is the extent to which the concentrations of the reactants affect the rate of a reaction, as shown in equation 5.5. Rate equation for DBDS degradation is given by,

\[
\frac{Rate}{k[DBDS]^{n}} = -\frac{d[DBDS]}{dt} = k[DBDS]^{n}
\]

(5.5)

Where \([DBDS]\) is the concentration of DBDS in ppm, ‘t’ is time in hours; \(k\) is the rate constant and ‘n’ is the order of the reaction.

The reaction rate of a zeroth-order reaction is independent of the concentration of the reactants and the reaction rate of a first-order reaction is directly proportional to the concentration of one reactant, even if more than one reactant is present. Similarly, the reaction rate of a simple second-order reaction is proportional to the square of the concentration of one of the reactants. Knowing the rate law of a reaction or by mathematical modeling of the experimental data, it is possible to understand the reaction mechanism involved. In this study, the rate of degradation of DBDS has been studied using these approaches with the objective of understanding how DBDS undergoes degradation in mineral oil during the service life of transformers.

By understanding the reaction rates, it would be possible to prevent building up of concentration of DBDS in mineral oil and also check the formation of copper sulphide which is a semi-conducting material and its accumulation in the paper winding of copper conductor leads to electrical discharges, thermal imbalance, and increase in current and ultimate failure of the insulation system of transformers. The objective of this work was to understand the degradation of DBDS in mineral oil and to effectively use the data in evolving mitigation techniques to combat the problem of copper corrosion in transformers. Though there is limited published data [9, 10] on measurement of reaction rates, these studies are based on small quantities of oil and restricted duration of thermal ageing, which was around 200 hours. However, keeping the service conditions in which power transformers work, this study has been carried out on long term basis, up to about 2000 hours, using much larger volumes of oil.

One of the previous approaches [9] used quadratic least square fit of \(\ln([DBDS]/[DBDS]_0)\) as a function of time for oil samples containing DBDS of initial concentrations of 3, 6, 9, 12 and 15 ppm at 150 °C. Double logarithm of \(\ln\)
\(\frac{d[DBDS]}{dt}\) versus \(\ln[DBDS]\) results in a straight line of which gives order ‘n’ from its slope and the intercept gives the value of \(\ln k\). The authors have reported that the approach was difficult to apply even at a lower concentration of 3 to 15 ppm involving small duration of 170 hours. Therefore, a new approach is attempted in this study, where thermal ageing duration is fragmented into different time periods for better understanding of order of reaction and its variations due to progressive thermal ageing.

Study of kinetics is also extended to thermal degradation of DBDS in presence of metal passivators. Passivators react with copper surfaces and from a protective covering to prevent the reaction of sulphur on copper [10-13]. Hence it is possible to understand degradation of DBDS when its action during thermal ageing on copper surface is avoided.

5.2 EXPERIMENTAL METHOD

Transformer oil containing DBDS of different concentrations ranging from 10 to 400 ppm was aged at different temperatures from 100 and 150 °C, in laboratory hot air oven. The pigtail specimens explained in chapter 3 under section 3.2.3. The pigtail specimen and mineral oil were separately dried at 90 °C under vacuum of 0.001mm of Hg for 72 hours. The pigtail samples were then impregnated with mineral oil and maintained at the same temperature and vacuum for a period of 48 hours. Oil samples containing different concentrations of DBDS are aged at specified temperatures for durations up to 2000 hours. The samples were also aged in limited air supply by purging nitrogen continuously to mimic conditions of a sealed transformer.

Transformers are of free breathing type where mineral oil undergoes ageing in oxygen or sealed transformers, where there is no oxygen supply. Therefore the reactions that take place under these two conditions are entirely different. Hence thermal ageing was carried out under nitrogen purging and in air to study the effect of these two conditions on the degradation mechanisms involved.

5.3 RESULTS AND DISCUSSIONS

In order to understand the kinetics of thermal degradation of DBDS in transformer oil which was thermally aged in presence of paper wrapped copper conductors, oil
samples with pigtail specimens were aged in air and under nitrogen purging at different temperatures.

5.3.1 Kinetics of degradation of DBDS at temperatures of 100 and 130 °C in nitrogen

The results of thermal ageing of DBDS of concentrations 50 to 300 ppm in transformer oil for duration of 2000 hours at a temperature of 100°C is shown in figure 5.1.

![Graph showing variation in concentration of DBDS with thermal ageing at 100 °C](image)

**Figure 5.1** Variation in concentration of DBDS with thermal ageing at 100 °C

A different trend in variation of concentration with ageing time is observed for different concentrations of DBDS. There is decrease in concentration of DBDS up to 204 hours of ageing for initial concentration of 50 and 100 ppm and in case of 200 and 300 ppm of DBDS, decrease in concentration is observed during the first 24 hours after which there is an increase in concentration of DBDS till 873 hours of ageing time in all the cases. Thus, the first DBDS concentration minimum in case of 50 and 100 ppm appears at 204 hours and it decreases by nearly 1/8th times to 24 hours when initial concentration of DBDS increases above 200 ppm. Thus the initial decrease in concentration with thermal ageing duration is a function of initial concentration and with higher initial concentration, rate of decrease in concentration appears much faster. The observed increase in concentration beyond its initial concentration of DBDS with 200 and 300 ppm was
attributed to the process of impregnation of the samples in oil for 48 hours before thermal ageing. The samples were prepared with 50, 100, 250 and 350 ppm of DBDS in oil. Considering initial impregnation of pigtail sample with oil as a part of the ageing cycle, the concentration of DBDS at the beginning of thermal cycle is observed to be around 50, 100, 250 and 350 respectively.

Variation of concentration of DBDS with ageing time for oil samples aged at 130 °C in nitrogen is shown in figure 5.2. There is a uniform trend in variation of concentration of DBDS with thermal ageing time. There is a decrease in concentration of DBDS when aged at 130 °C and the first minimum in concentration is observed around the 176 hours for all concentrations of DBDS. Thereafter, the concentration starts increasing up to about 436 hours when the maximum is reached and it decreases thereafter.

![Figure 5.2 Variation in concentration of DBDS with thermal ageing at 130 °C](image)

The order of the reactions are obtained by iterative method by plotting concentration of DBDS as a function of time for zero order, natural logarithm of concentration versus time for first order and inverse of concentration versus time for second order.

The order of thermal degradation of DBDS is computed by considering the initial 180 hours of thermal ageing. Since the ageing duration in the present study is around 700 hours, it is difficult to determine the order of the reaction based on the entire thermal
cycle and hence the experiments were repeated by limiting the ageing to 176 hours. The variation of concentration with time is shown for a period of 176 hours in figure 5.3. The results clearly indicate that a linear least square fits the degradation data of DBDS with ageing time at 130 °C till the 176 hours of thermal ageing. The computed values of rate constant \( k \) and correlation coefficient \( (R^2) \) are shown in table 5.1. Average rate constant obtained for the samples aged at 130 °C for 180 hours is 0.0026 mg L\(^{-1}\) h\(^{-1}\).

\[ \text{Table 5.1 Rate constant and correlation coefficient obtained from figure 5.3} \]

<table>
<thead>
<tr>
<th>Initial concentration of DBDS (ppm)</th>
<th>( k ) ( (\text{h}^{-1}) )</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.0027</td>
<td>1</td>
</tr>
<tr>
<td>50</td>
<td>0.0025</td>
<td>0.9975</td>
</tr>
<tr>
<td>100</td>
<td>0.0026</td>
<td>0.9981</td>
</tr>
<tr>
<td>150</td>
<td>0.0025</td>
<td>0.9923</td>
</tr>
<tr>
<td>200</td>
<td>0.0027</td>
<td>0.9999</td>
</tr>
<tr>
<td>300</td>
<td>0.0027</td>
<td>0.9954</td>
</tr>
</tbody>
</table>

G.A Oweimreen and co-workers [9] have observed that DBDS of initial concentrations 6,9,12 and 15 ppm in mineral oil when thermally aged at 150 °C, in presence of copper conductors, follow first order kinetics till 170 hours of ageing with an
average rate constant of $0.0129 \pm 0.002 \text{ mg L}^{-1}\text{h}^{-1}$. The difference in rate constant observed between published data and present work is due to changes in temperature, sample preparation, sample size, the method of ageing and the method of sampling.

Because of the complexity of the reactions, it was difficult to determine rate of reaction which was the best fit for at all points of the graph. It is expected that the order of the reaction should remain same irrespective of the starting concentrations. However, the effect of many experimental parameters like adsorption of DBDS on surface of paper, competing mechanisms between thermal degradation of DBDS, recombination of radicals and degradation of DBDS in presence of copper during thermal ageing make the determination of the order of reaction a difficult task.

The degradation of DBDS at 100 °C is repeated separately from 0 to 873 hours of thermal ageing and from 873 to 1899 hours of thermal ageing in order to understand the variations and to fit appropriate mathematical equations to represent the reaction rate involved. Data from 0 to 873 hours of ageing was analysed for determining order by plotting them in different ways which are discussed earlier. However, it was not possible to fit an equation for this initial period of ageing and this indicates that the complex reactions take place where as a linear least square fit for degradation of DBDS as a function of time at 100 °C from 873 to 1899 hours was possible and is shown in figure 5.4. Though straight line with a negative slope is observed indicating zero order kinetics,
the plots for different concentrations are not parallel and hence slopes obtained are not constant. Therefore an attempt to arrive at a single equation to represent the entire process of thermal degradation was not successful.

A linear least square fit for data of degradation of DBDS with ageing time at 130°C, from 436 to 676 hours of thermal ageing is shown in figure 5.5. The variation in concentration of DBDS with time is also a linear fit, indicating zero order kinetics but even in this case, the slope of the plots are inconsistent.

![Figure 5.5 Linear least square fits showing depletion of DBDS with time at 130°C from 436 to 700 hours](image)

5.3.2 Kinetics of degradation of DBDS at 100 °C in air

Thermal ageing of transformer oil having DBDS in air follows different trend. Presence of oxygen or oxygen donating compounds aid the formation of CuO. The CuO reacts with thiols, thiolate radicals and thiolate anionios to form Cu₂S [14].

\[
2RSH + CuO \rightarrow (RS)_2Cu + H_2O \tag{5.6}
\]

\[
2Cu(SR)_2 \rightarrow 2CuSR + RSSR \tag{5.7}
\]

\[
2CuSR \rightarrow Cu_2S + RSR \tag{5.8}
\]

The results of thermal ageing of mineral oil with DBDS in air terms of decrease in concentration are shown in figure 5.6. Here a linear least square fit matches the entire degradation data and the trend in results clearly show that degradation of DBDS of
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concentration 50, 100, 200 and 300 ppm as a function of time, at a temperature of 100˚C in air follows the trend seen under nitrogen purging at 130˚C. However, there is a continuous decrease in concentration of DBDS up to 1000 hours of ageing, unlike thermal ageing in nitrogen. It is interesting to observe that the peak due to recombination of radicals was not visible at any point of thermal ageing and the degradation follows zero order kinetics with a negative slope. This is mainly due to the long cycles of thermal ageing selected wherein it is difficult to identify the point at which peak can appear. Rate constant and correlation coefficients obtained are shown in table 5.2. Average rate constant obtained is 0.0021 mg L\(^{-1}\)h\(^{-1}\).

![Figure 5.6 Linear least square fits showing depletion of DBDS with time at 100˚C in air](image)

<table>
<thead>
<tr>
<th>Initial concentration of DBDS (ppm)</th>
<th>k (h(^{-1}))</th>
<th>R(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0.0021</td>
<td>0.9950</td>
</tr>
<tr>
<td>100</td>
<td>0.0019</td>
<td>0.9991</td>
</tr>
<tr>
<td>200</td>
<td>0.0022</td>
<td>0.9934</td>
</tr>
<tr>
<td>300</td>
<td>0.0020</td>
<td>0.9947</td>
</tr>
</tbody>
</table>
Though rate constant is independent of concentration of the reactants, under given conditions of thermal ageing, the reactants involved or other factors contributing to the degradation of DBDS in oil which is thermally aged in presence of paper covered copper conductors is different at different stages of thermal ageing of mineral oil. It is essential to remember that different conditions like effective concentration of DBDS, area of availability of copper ions in oil are all different. Hence when long duration of ageing is carried out, the mechanisms involved make it very complex while attempting the determination of rate constants.

5.3.3 Kinetics of degradation of DBDS at 150 °C in presence of passivators

To suppress corrosion of copper conductors from attack by DBDS, metal passivators and deactivators are used. The passivators or deactivators form a film on the copper surface and thus protect copper from attack by DBDS [11-13]. Since it was difficult to arrive at the reaction rate constants of thermal ageing of mineral oil with DBDS, the study was repeated in presence of metal passivators which suppresses the effects of DBDS on copper. It would be interesting to understand how DBDS would degrade in presence of metal passivators or deactivators. For this purpose, 100 ppm of Irgamet 39 and BTA metal passivators were added to mineral oil and simultaneously DBDS of different concentrations were used. The pigtail specimens were aged in mineral oil which has 100 ppm DBDS and 100 ppm Irgamet 39 or BTA. It is expected that both DBDS and passivators would take time to be adsorbed or absorbed by paper and then would reach the copper surfaces. The moment the passivators are able to form a protective layer on copper, the reaction of DBDS on copper conductors would be prevented. It would be interesting to observe the changes that kinetics of DBDS degradation would undergo in presence of metal passivators.

The effect of thermal ageing of mineral oil at a temperature of 150 °C in presence of Irgamet 39 and BTA, from 0 to 800 hours is shown in figure 5.7. Degradation of DBDS is similar both in presence of Irgamet 39 and BTA. There is an initial decrease in DBDS concentration up to 160 hours of thermal ageing followed by a slight increase around 280 hours of ageing. This is the period when DBDS is able to attack copper and it appears that Irgamet 39 takes longer duration to act on copper. Hence an initial increase in
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concentration of DBDS is observed. However, concentration of DBDS decreases to 48 ppm in case of Irgamet 39 and 47 ppm in case of BTA after 798 hours of ageing.

It is possible to fit a linear least square curve to represent the degradation of DBDS from 0 to 160 hours as a function of ageing duration. Degradation of DBDS in presence of passivators follows zero order kinetics from 0 to 160 hours of ageing with an average rate constant of 0.090 mg L\(^{-1}\)h\(^{-1}\).

This result clearly indicates that it would be preferable to use Irgamet 39 or BTA passivator much before commissioning of transformers and in such cases, even if DBDS is present or formed accidentally, it would undergo degradation without affecting the copper surfaces. This will be more effective than adding Irgamet 39 midway during the service life of transformers.

![Degradation of DBDS with time at 150°C in presence of passivators](image)

**Figure 5.7** Degradation of DBDS with time at 150°C in presence of passivators

### 5.4 Activation Energy

Activation energy \((E_a)\) is calculated for degradation of DBDS in presence of nitrogen as well as in air. Activation energy can be calculated from the value of \(E_a / R\) which is obtained by plotting \(\ln \) (rate) versus inverse of temperature in kelvin as reported in literature [10]. Authors have arrived at the equation (5.9) from which activation energy can be calculated.

\[
\ln \text{ (rate) } = \ln B - E_a / RT
\]

(5.9)
Where, B is constant if initial concentration of copper and DBDS in all the samples are same and R is gas constant equal to 8.3143 J K$^{-1}$ mol$^{-1}$.

Table 5.3 furnishes the parameters used to calculate $E_a$ in nitrogen. Activation energy for the degradation of DBDS in nitrogen can be obtained from figure 5.8.

**Table 5.3 Parameters used to calculate $E_a$ in nitrogen**

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>1/T (K$^{-1}$)</th>
<th>ln (rate)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>2.68 × 10$^{-3}$</td>
<td>-2.3439</td>
</tr>
<tr>
<td>130</td>
<td>2.481 × 10$^{-3}$</td>
<td>-0.59111</td>
</tr>
<tr>
<td>140</td>
<td>2.421 × 10$^{-3}$</td>
<td>-0.1824</td>
</tr>
</tbody>
</table>

![Figure 5.8 Activation energy of degradation of DBDS in nitrogen in presence of copper](image)

Table 5.4 gives the parameters used to calculate $E_a$ in nitrogen. Activation energy for the degradation of DBDS in air can be obtained from figure 5.9. Hence, activation energy for the degradation of DBDS in nitrogen is 70 kJ/mol and for reactions in oxygen, it is 45 kJ/mol.

**Table 5.4 Parameters used to calculate $E_a$ in air**

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>1/T (K$^{-1}$)</th>
<th>ln (rate)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>2.68 × 10$^{-3}$</td>
<td>-2.4135</td>
</tr>
<tr>
<td>135</td>
<td>2.45 × 10$^{-3}$</td>
<td>-1.2535</td>
</tr>
<tr>
<td>150</td>
<td>2.364 × 10$^{-3}$</td>
<td>-0.6668</td>
</tr>
</tbody>
</table>
Results indicate that in presence of nitrogen, DBDS reacts only with copper and in oxygen there is a simultaneous reaction both with air and copper. This may be the reason for higher activation energy in presence of nitrogen as compared to oxygen.

5.5 Practical implications of the study

The mechanism and kinetics of degradation of DBDS and formation of copper sulphide in power apparatus was complex in nature since the reactions involve some dependent and few independent parameters in addition to temperature and concentration of reactants. It is difficult to analyze and compare the published data with present work due to lack of standard procedures of thermal ageing, sampling size and sampling duration, volume of oil and the methods of analysis. Some of the areas which could be standardized to improve inter laboratory comparison of results of thermal ageing are as follows.

1. Conditions of sample ageing: In this study, thermal ageing was carried out in specially designed glass bottles of 500 ml capacity and for longer ageing durations ranging from 600 to 2000 hours whereas in literature, the thermal ageing is carried out in small vials using smaller volumes for ageing duration of about 200 hours and in majority of cases a headspace device was used. Though such methods ward off the uncertainties due to sample cooling, exposure to air
and likely moisture absorption and interruption of thermal ageing, larger volume of oil is used and the duration of ageing is carried out for much longer durations and hence better correlation of results to service conditions is possible. Both the methods have resulted in important conclusions which are useful for transformer maintenance.

2. **The method of purging nitrogen** continuously to create situation that exists in sealed transformers has certain disadvantages; especially during removal of oil for analysis, the sample is exposed to air. The ageing cycles in long duration ageing can vary anywhere between 10 to 15 cycles and this factor increases the probability of exposure of oil to air. In spite of maximum care being undertaken, results are likely to be affected by oxygen and hence results of experiments using smaller quantities in headspace device and larger volumes using nitrogen purging give different results. A new method which uses the advantages of these two methods would be preferable.

3. **Adsorption of DBDS by paper layers** and the time delay involved in adsorption of metal passivators by paper and formation of protective layer in copper conductors are not studied and understood. These aspects need further investigations and better understanding of these aspects can result in better analysis of kinetics of thermal degradation of DBDS in mineral oil.

4. **Adsorption of DBDS-Cu complex** by paper layers and on copper surface results in determination of only partial concentration of DBDS (DBDS in oil) and determination of real concentration of DBDS in the insulation system is difficult.

5. **Adsorption of DBDS** initially also leads to serious errors in finding the initial concentration of DBDS. When samples are prepared by conventional vacuum impregnation, this problem looks very complex and considerable reductions in DBDS concentration, followed by increase in concentration of DBDS are observed. Hence, DBDS should be added for laboratory studies only after vacuum impregnation and not before.

6. Even in air, increase in DBDS concentration as in nitrogen would occur but it is difficult to detect these changes when thermal ageing cycles are of longer durations. This aspect is discussed in chapter 4 on thermal degradation of DBDS.
Similarly, the concentration of DBDS when recombination of radicals occurs is the net result of degradation of DBDS and increase in concentration of DBDS due to recombination. Thus two reactions namely thermal degradation of DBDS and recombination of radicals to form DBDS become competing processes and hence uncertainties are likely to affect the net results.

5.6 CONCLUSIONS

The following are the important conclusions of the study:

1. Degradation of DBDS in thermally aged transformer oil in presence of paper wrapped copper conductor is a complex reaction. It involves both degradation and reformation of DBDS at different stages of thermal ageing. Hence reaction rate would depend on the reactions occurring and a general trend to describe the mechanism of degradation of DBDS is difficult due to complex reactions involved.

2. Kinetic studies of the reaction rates involved in thermal degradation of DBDS is very complex because of many parameters involved in the process like thermal degradation of DBDS, degradation of DBDS in presence of copper which is a function of time, recombination of radicals to form DBDS which is again a time dependent parameter, formation of DBDS-Cu complex, release of copper ions in oil and formation of Cu$_2$S and its release from copper surface.

3. Supply or availability of oxygen has significant effect on rate of the reaction and hence experiments should incorporate methods to eliminate the effect of oxygen completely if actual sealed transformer conditions are to be replicated.

4. The thermal degradation of DBDS is satisfactorily explained over certain time zones of thermal ageing and it is difficult when complex reactions take place leading to radical formation, radical recombination, flaking of copper sulphide from copper conductor which permit more DBDS to react with copper.

5. In the time zones selected for thermal ageing of mineral oil containing DBDS, it is observed that the reactions are of zero order and first order and this is in agreement with the published data. Hence it is most likely that the order of reaction would undergo changes during the thermal ageing cycles in transformers. Because of the uncertainty of rate of reaction, removal of DBDS or passivation of
mineral oil would be a better solution for mitigation of copper corrosion due to DBDS.

6. Contrary to the general belief, long duration thermal ageing of mineral oil with DBDS at 100 °C seems to be equally dangerous because of the uncertainties in reaction rate and order of reaction during long term ageing. The period of uncertainty decreases with increase in temperature.

7. Activation energy is calculated for degradation of DBDS in presence of nitrogen is 70 kJ/ mol and for reactions in oxygen it is 45 kJ/ mol.

REFERENCES

1. CIGRE TF A2. 32-03, “Sulphur speciation in insulating oil-Final report”, 2010


