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# Kinetics of the release of antimony trioxide from the backcoated textile preparation

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ABSTRACT

Segregation of antimony trioxide (ATO) from back-coated textiles was studied for two types of textile samples: A (ATO-Hexabromocyclododecane) and B (ATO-Decabromodiphenyl ether). Samples A was found to lose 5.3, 12, 28 and 39 %*wt*:*wt* of the amount of ATO originally present due to thermal ageing and UV exposure, respectively. Thermal ageing was performed at 25, 60 and 90 °C compared to 11.0, 17.3, 26.0 and 20.4 % *wt*:*wt* of ATO for sample B. The release follows first order kinetics with rate constants of $7.59\times10^{-3}$, $1.89\times10^{-2}$, $4.80\times10^{-2}$ and $2.60\times10^{-2}$ day$^{-1}$, respectively, for type A and $9.20\times10^{-3}$, $2.06\times10^{-2}$, $4.10\times10^{-2}$ and $3.83\times10^{-2}$ day$^{-1}$ for type B aged at 25, 60, 90 °C and UV exposure, respectively. Migration of ATO from the backcoated textile into simulated biological fluids was also studied for different type of samples under different ageing conditions using Head-over-Heels and contact blotting tests. The presence of biological fluids enhances the migration of ATO.

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## 1. Introduction

Flame retardant (FR) materials could be defined as chemicals used to prevent or at least delay the spread of fire through disrupting the combustion step of a fire cycle, this can be done by delaying the time of flashover by slowing down the initial burning rate [1]. FR material used mainly in consumer products (i.e., furniture, textiles, electronics, and insulation, etc.). Normally, they are incorporated into the consumer products either by adding them during the manufacture process or even after (i.e., backcoated textile) [2-5]. Halogenated FR materials are often the most effective flame retardant when both performance and cost are considered [6-9]. However, despite the proven rule of their function as FR, there is an environmental and health concern about their use [10-14]. Moreover, usages of halogenated FR require the addition of high percentage of FR to ensure an effective action; on the other hand, it is known that the addition of small percentage of inorganic FR such as antimony trioxide not only reduces the addition level of halogenated FR in consumer products but also significantly enhances their activity.

Antimony trioxide (ATO) is an inorganic FR that does not act as flame retardant by its own; it acts as synergists to increase the efficiency of halogenated FR. The combination of halogenated FR with ATO is a typical case of effective synergism which enhances the efficiency of halogenated FR. Moreover, conjugation of halogenated FR with ATO is favored since it allow to use lower concentration of halogenated FR which reduces environmental concerns and improve the properties of products in which FR were incorporated in (i.e., plastics, rubbers, textiles, paper and paints) [15].

Literature proposes different mechanisms to explain the synergetic behavior of ATO, in summary ATO reacts with halogenated FR to form a very reactive intermediate, antimony oxychloride, which reacts further to form antinomy trichloride, these compounds generate the FR function and reduce the spread of flames [16].

Halogenated FR and ATO were added to textile during its manufacturing process (i.e., in backcoated textile) and they were physically combined to the textile. Therefore, they can easily leach or migrate out of textile and could be absorbed by contact bodies. Consumer Product Safety Commission (CPSC) reported that 0.8 mg of antimony will be absorbed daily just from our mattresses.

Absorption of ATO by skin could cause many problems; it was reported by united state environmental protection agency; that short term exposure to antimony results in eye and skin irritation and lead to what is called antimony spots [17]. Furthermore, oral exposure to antimony in humans has results in gastrointestinal effects [18,19], prolonged exposure


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may damage the liver and the heart muscle [20]. Finally serious health effects were also attributed to the direct contact with ATO, which could be summarizing as follow [20]:

1) It may cause heart to beat irregularly or stop,
2) A reproductive defects in humans (i.e., spontaneous abortions, a reproductive effects and failure to conceive in animals) [20],
3) Antimony exposure appear to target the respiratory and cardiovascular systems [21],
4) Moreover, reports revealed that after several days of exposure of ATO traces of antimony were found in the blood and urine [22],
5) Finally, it was reported through systemic studies that ATO is absorbed dermally in rabbits [23,24].

Recently, we studied the kinetics of thermal and photolytic degradation of hexabromocyclododecane (HBCD) and decabromodiphenyl ether (DBE 209) and its migration into biological fluid from the backcoated textile [2,25-27]. Moreover, we previously introduce a simple and reproducible analytical method for determination of ATO from backcoated textile [26].

In this manuscript, we present the study of segregation of FR from the backcoated textile through investigation of the kinetics of the release of ATO from the backcoated textile preparation. Also, in this paper, we are going to evaluate the behavior of two fire-retarded fabrics to which fire retardants have been added to a back coating each contained ATO, but with different brominated fire retardants.

The strategy of investigation the rate of the release of ATO from the backcoated textile samples is summarized as follow: The initial ATO loading was determined. Specimens of the fabrics were then exposed to elevated temperatures or fluorescent lighting, and then to artificial sweat or saliva, simulating the effect of the biological fluids. The kinetics of thermal and photolytic release of ATO from the backcoated textile formulation as well as its migration into biological fluids will also be studied using the validated analytical methods [26].

Since ATO normally coexist with other halogenated FR two different back-coated textile samples each contained ATO with different concentration were analyzed.

## 2. Experimental

### 2.1. Chemicals and reagents

ATO, $Sb_2O_3$ (>99% Sigma-Aldrich), was used without further purification. Distilled water was used throughout the experiment. All chemicals used to prepare different solutions and artificial biological fluids were purchased from Sigma-Aldrich and used without further purification.

A representative cotton fabric with defined and known backcoating formulation containing: hexabromocyclododecane /antimony trioxide (3.6% by weight) type A textile and textile containing 4.3% by weight of antimony trioxide and decabromodiphenyl ether (type B, BDE 209/ATO) were used in this study.

### 2.2. ATO extraction and analysis from the backcoated textile sample

ATO was extracted from the fabric samples (around 2 g) using 5 N HCl solution [26]; the samples were there by extracted for 6 hours under shaking conditions and then 1 hour on ultrasonic bath. The extracted solutions were filtered and diluted then the samples were analyzed on Unicam 929 Atomic absorption system equipped with hallow-cathode lamp of antimony at 206 nm and a cap type cuvette. The weight of the textile was recorded before and after extraction. Detailed extraction and analytical methods were investigated earlier [2,26]. Validation of the analytical and the extraction methods described earlier [1,26]. The method include; study of the repeatability of analytical method and extraction methods, determination of the linear range by dilution of standard solutions, then estimation of the limit of quantification using standards, and finally, spike each matrix that is subject to extraction to determine the recovery of each extraction method, and compare with blanks [1,2], as a result a complete and validated analytical method for both extraction and analytical method was produces with linear calibration curve in range of 5 to 220 ng with detection limit of 5 ng [26].

### 2.3. Kinetic measurements

Kinetic measurements were carried out by monitoring the recovered percentage of ATO from the back-coated textile *vs* the period of ageing at different temperatures [2]. The concentration of the released ATO was measured using spectrophotometric methods. The rate constants of the release process were obtained by non-linear least-square fitting of the concentration-time data to equation (1) [2]:

$$A_t = A_0 e^{-kt} \quad (1)$$

where $A_t$ and $A_0$ are the concentrations of ATO at time t and time zero, respectively, and k indicates the rate constant of the release process [2] (in fact, the data were tested for different kinetic model, and it was found that concentration is exponentially changed with time and the data were fitted according to equation (1), which is typical equation for the first order reaction, on the other hand, the attempt to fit the data to the different kinetic models was failed [2])

Determination of the thermodynamics parameters was obtained using Eyring equation (Equation (2)); the obtained rate constants ($k_{obs}$) were fitted to Eyring equation (Equation (2)):

$$\ln\left(\frac{k_{obs}}{T}\right) = -\frac{\Delta H^*}{R}\cdot\frac{1}{T} + \ln\left(\frac{k_B}{h}\right) + \frac{\Delta S^*}{R} \quad (2)$$

where $k_{obs}$ is observed rate constant of the release process at absolute temperature (T). R, $k_B$ and h are gas constant, Boltzmann constant and Planck's constant, respectively.

### 2.4. Thermal ageing

Three specimens (300 × 80 mm) of textile samples containing ATO were used for each test, samples were placed in an oven maintained at fixed temperature with a circulating fan. After each ageing experiment, samples were kept in sealed freezer bags and stored at -18 °C until tested. Three different temperatures were used for ageing conditions: 90, 60 and 25 °C for whole period of 200 days. Samples for kinetic study were taken in regular intervals depending on the ageing conditions [2,25,27].

### 2.5. UV ageing

A UVA apparatus with irradiation intensity of 1.25 W/m², provides the maximum convenient level for the UVA-340 lamp, was used. Samples were uniformly exposed to fluorescent light for a whole period of 200 days and sampled every five days [2,25,27].

### 2.6. Migration into biological stimulants

Simulation of the exposure of flame retardants by skin and oral exposure related to repeat sucking of upholstery furniture were studied using the contact-blotting extraction, and the Head-over-heels methods [2], the two methods were validated using the following strategy: (a) study of the repeatability of extraction method with at least three replicates,

**Table 1.** Results of the extraction of the thermally aged fabric textile samples, Type A (ATO-HBCD) samples, at the end of ageing period.

| Sample | Sample weight (mg) | Weight lost [1] (mg) | Theoretical [2] ATO (mg) | Recovered ATO [3] (mg) | Recovery [4] (%) |
|---|---|---|---|---|---|
| *Samples aged at 25 °C for 200 days* | | | | | |
| Blank | 112.0 | 3.3 | 0.0 | 0.0 | 0.0 |
| Blank | 114.0 | 3.7 | 0.0 | 0.0 | 0.0 |
| 1 | 132.1 | 13.5 | 4.756 | 4.1±0.6 | 86.0 |
| 2 | 137.2 | 13.9 | 4.939 | 4.0±0.3 | 81.4 |
| 3 | 135.4 | 14.1 | 4.874 | 4.4±0.4 | 89.6 |
| Mean recovery: 85.7±4.1% | | | | | |
| *Samples aged at 60 °C for 200 days* | | | | | |
| Blank | 112.7 | 5.2 | 0.0 | 0.0 | 0.0 |
| Blank | 111.9 | 6.2 | 0.0 | 0.0 | 0.0 |
| 1 | 135.4 | 14.4 | 4.874 | 3.8±0.1 | 77.6 |
| 2 | 137.2 | 15.1 | 4.939 | 3.9±0.6 | 79.7 |
| 3 | 134.4 | 14.6 | 4.838 | 3.8±0.4 | 79.3 |
| Mean recovery: 78.9±1.1% | | | | | |
| *Samples aged at 90 °C for 200 days* | | | | | |
| Blank | 143.9 | 6.7 | 0.0 | 0.0 | 0.0 |
| Blank | 142.1 | 3.4 | 0.0 | 0.0 | 0.0 |
| 1 | 125.1 | 12.6 | 4.503 | 3.1±0.4 | 68.5 |
| 2 | 135.4 | 13.3 | 4.874 | 2.8.±0.1 | 58.2 |
| 3 | 130.5 | 15.4 | 4.698 | 2.9±0.8 | 62.5 |
| Mean recovery: 63.0±5.1% | | | | | |

[1] Weight lost due to ageing condition.
[2] Fabric samples contain 3.6% by weight of Antimony trioxide for ATO-HBCD.
[3] Results are averaged of three repeated samples.
[4] Percentage of ATO recovered compared to theoretical concentration of antimony trioxide contained on the fabric sample.

(b) Spike some matrix that is subject to extraction to determine the recovery of each extraction method, and compare with blanks [2,25,27].

### *2.6.1. Contact-Blotting extraction [2]*

The extractions were performed using a method adapted by CPSC [18]. A piece of (2×2 cm) textile, which had been previously dried in a desiccator and weighed, was placed in a 90 mm diameter Petri dish. 2 mL of the extraction fluid (i.e., distilled water, artificial saliva… etc.) was added to the fabric, the fabric was then covered with a circular filter paper (cellulose filter paper, Whatman) (which had also been stored in a desiccator) of diameter 5.5 cm (both the fabric and the filter paper were saturated). The dish was left in the fume cupboard until both the filter paper and the fabric were completely dried. Both the fabric and the filter paper were then stored in a desiccator before weighing them, then the FR present in the dry filter paper was extracted and analyzed. Results are the average of at least three replicates [2].

### *2.6.2. Head-over-Heels extraction*

A piece of fabric (2.5 × 2.5 cm), which had been previously dried and weighed just before use, was placed in a 25 mL screw-cap bottle [2]. 25 mL of the extraction fluid (i.e., distilled water, artificial saliva… etc.) was added and the closed bottle was rotated at 60 rpm for 30 min. The fabric was then removed and placed in another bottle containing 25 mL of fresh solution; the bottle was then rotated for another 30 min [2]. The Head-over-Heels extraction was then repeated one more time. Before reweighing, both the fabric and the filter paper were stored in a desiccator to ensure that both were dry. The solutions obtained from the three extractions were combined and analyzed [2,25,27].

### *2.6.3. Artificial biological fluids [2]*

Since migration of the FR from the textile material to humans could be accelerated by the presence of biological fluids; Skin and oral exposure of FR were studied under the effect of different artificial biological fluids; water, artificial saliva, artificial perspiration and 5% citric acid (chosen to simulate acid, food, or beverages, orange juice). The artificial biological fluids were prepared as follow:

Artificial saliva solution was prepared by mixing the following mole fractions of the reagents ($\chi$ = (mole of reagent A)/( $\Sigma$ mole of all reagents)): magnesium chloride (0.08), potassium carbonate (0.15), potassium chloride (0.4), potassium phosphate (0.13), sodium chloride (0.2) and potassium chloride (0.04). The pH of the solution was adjusted to 6.8 with diluted HCl [2].

Artificial sweat solution was prepared by mixing the following reagents: *Tris*(hydroxymethyl)aminomethane, 5 g, nitrilotriacetic acid (NTA), 0.5 g, sodium chloride, 5.0 g and urea, 0.5 g in 1 L deionized water. The pH was adjusted to 8±0.1 with diluted HCl. Citric acid solution was prepared by dissolving 5 g of citric acid in 100 ml of deionized water.

## 3. Results and discussion

For the purpose of this study, two type of backcoated textile samples were used, type A which contain combination of ATO with hexabromocyclododecane (ATO-HBCD, contain 3.6% %*wt*:*wt* of antimony trioxide) and type B which contain ATO with decabromodiphenyl ether (BDE 209, ATO-BDE 209 contain 4.3 % of ATO). Back-coated textile samples were analysed for their content of ATO [26]. The analysis of the unaged textile samples revealed that they contained ~91%*wt*:*wt* of the claimed concentration of ATO in Type A (ATO-HBCD) samples compared to ~70 %*wt*:*wt* of the theoretical concentration of ATO claimed to exist in type B backcoated samples. Samples of the same textile were then thermally aged or exposed to UV light at 340 nm for different periods of time[1,2]; at the end of the ageing period, samples of both types, A and B, were analysed and their ATO content was determined. Table 1 and 2 show the results of the complete extraction of the thermally and UV aged samples at the end of the ageing period, these results indicate that the total recovery of antimony trioxide concentrations decreased due to ageing conditions (like other brominated FR) [1,2].

A direct comparison of the weight loss with the blank samples (i.e., samples containing no flame retardant) and the ones containing (FR) revealed that the main source for the weight loss of the thermally or UV aged textile samples can be attributed to the release of FR [1,2], which matched with similar results obtained in literatures [2,25], from the present results and taken into accounts mass balance we can conclude that the total weight loss is attributed to the loss of both halogenated FR and ATO [2,25].

**Table 2.** Results of the extraction of the thermally aged fabric textile samples, Type B (ATO-DBE209) samples, at the end of ageing period.

| Sample | Sample weight (mg) | Weight lost [1] (mg) | Theoretical [2] ATO (mg) | Recovered ATO [3] (mg) | Recovery [4] (%) |
|---|---|---|---|---|---|
| *Samples aged at 25 °C for 200 days* | | | | | |
| Blank | 112.0 | 3.3 | 0.0 | 0.0 | 0.0 |
| Blank | 114.0 | 3.7 | 0.0 | 0.0 | 0.0 |
| 1 | 125.4 | 12.1 | 5.392 | 3.5±0.5 | 64.4 |
| 2 | 131.5 | 14.2 | 5.654 | 3.6±0.8 | 63.8 |
| 3 | 128.3 | 13.1 | 5.517 | 3.7±0.6 | 67.4 |
| Mean recovery: 65.2±1.9% | | | | | |
| *Samples aged at 60 °C for 200 days* | | | | | |
| Blank | 112.7 | 5.2 | 0.0 | 0.0 | 0.0 |
| Blank | 111.9 | 6.2 | 0.0 | 0.0 | 0.0 |
| 1 | 144.6 | 14.6 | 6.218 | 3.6±0.3 | 57.7 |
| 2 | 139.6 | 13.2 | 6.003 | 3.5±0.2 | 58.0 |
| 3 | 148.7 | 16.4 | 6.394 | 3.7±0.5 | 57.4 |
| Mean recovery: 57.7±0.3% | | | | | |
| *Samples aged at 90 °C for 200 days* | | | | | |
| Blank | 143.9 | 6.7 | 0.0 | 0.0 | 0.0 |
| Blank | 142.1 | 3.4 | 0.0 | 0.0 | 0.0 |
| 1 | 104.6 | 14.2 | 4.498 | 2.2±0.2 | 50.0 |
| 2 | 113.2 | 14.2 | 4.868 | 2.5±0.5 | 51.2 |
| 3 | 109.8 | 14.2 | 4.721 | 2.2±0.3 | 46.2 |
| Mean recovery: 49.1±2.6% | | | | | |

[1] Weight lost due to ageing condition.
[2] Fabric samples contain 4.3% by weight of ATO for ATO-BDE 209.
[3] Results are averaged of three repeated samples.
[4] Percentage of ATO recovered compared to theoretical concentration of ATO contained on the fabric sample.

**Table 3.** Results of total antimony trioxide extracted from the textile fabric samples, exposed to UV radiation.

| Sample | Weight (mg) | Weight lost [1] (mg) | Theoretical [2] $Sb_2O_3$ (mg) | Recovered [3] $Sb_2O_3$ (mg) | Recovery [4] (%) |
|---|---|---|---|---|---|
| *Blank sample* | | | | | |
| 1 | 143.0 | 3.8 | 0.0 | 0.0 | 0.0 |
| 2 | 215.6 | 8.8 | 0.0 | 0.0 | 0.0 |
| 3 | 181.6 | 2.5 | 0.0 | 0.0 | 0.0 |
| *Fabric sample containing ATO-HBCD* | | | | | |
| 1 | 104.1 | 14.6 | 3.748 | 2.10±0.07 | 56.3 |
| 2 | 110.2 | 13.4 | 3.967 | 1.96±0.09 | 49.4 |
| 3 | 132.1 | 14.8 | 4.756 | 2.40±0.03 | 50.4 |
| Mean recovery: 52.0±2.7% | | | | | |
| *Fabric sample containing ATO-BDE 209* | | | | | |
| 1 | 104.3 | 12.3 | 4.310 | 2.34±0.07 | 54.3 |
| 2 | 137.0 | 18.4 | 5.891 | 3.01±0.05 | 51.1 |
| 3 | 125.4 | 15.6 | 5.392 | 3.16±0.02 | 58.5 |
| Mean recovery: 54.6±3.3% | | | | | |

[1] Weight lost due to ageing condition.
[2] Fabric samples contain 3.6 and 4.3% by weight of Antimony trioxide for ATO-HBCD and ATO-BDE 209, respectively.
[3] Results are averaged of three repeated samples.
[4] Percentage of ATO recovered compared to theoretical concentration of ATO contained on the fabric sample.

### *3.1. Thermally aged samples*

ATO extracted at the end of the ageing period from the Type A (ATO-HBCD) textile samples aged at 25, 60 and 90 °C were found to be 85.7±4.1, 78.9±1.1 and 63.0±5.1%, respectively, for the theoretical concentration originally present in the unaged samples. These results indicate that ~5.3, 12.1 and 28.0% ATO were lost due to thermal ageing at 25, 60 and 90 °C, respectively, (i.e., analyse of the unaged textile samples of type A revealed that they contained ~91% *wt*:*wt* of the claimed concentration of ATO) Table 1.

On the other hand for Type B (ATO-BDE 209) textile samples; antimony trioxide extracted at the end of the ageing period at 25, 60 and 90 °C were found to be 65.2±1.9, 57.7±0.3 and 49.1±2.6%, respectively, for the theoretical concentration originally present in the unaged samples, which indicates that ~4.8, 12.3 and 20.9% ATO were lost due to the thermal ageing at 25, 60 and 90 °C, respectively,(i.e., analyse of the unaged textile samples of type B revealed that they contained ~70% *wt*:*wt* of the theoretical concentration of ATO claimed to exist), Table 2.

### *3.2. UV-aged samples*

Table 3, shows the results of the analysis of ATO extracting solutions from the textile fabric samples previously exposed to UV light (lamp at 340 nm, radiation intensity 1.25 W.m$^2$) for 200 days [1,2], for type A samples; the extracted antimony trioxide was found to be 52.0±2.7% of the theoretical concentration originally present in the unaged samples indicating that 38% had been lost due to UV exposure. For type B (ATO-BDE 209) samples; the extracted antimony trioxide was found to be 54.6±3.3% of the theoretical concentration originally present in the unaged samples indicating that 15.4% had been lost due to UV exposure.

### *3.3. Kinetic measurements*

Time dependence of the release of ATO from the thermally and UV aged samples were also studied [1,2]. Figure 1 and 2 show the recovered percentage of antimony trioxide from the back-coated textile versus the period of ageing at different temperatures, the data in the figures showed that the total concentration of ATO recovered from the back-coated textile decreases over time [1,2], albeit at different rates for both type of textile samples. The data were best fitted to first order kinetics according to Equation (1) [2] (i.e., concentration of the released antimony trioxide is exponentially changed with time, which characteristic of the first order reaction).

Table 4 shows the release rate constants of ATO under different conditions, the release rate constants are directly related to the ageing temperature: increasing the temperature seems to weaken the interaction between the (FR) and the textile which enhance the leach of ATO into the environment [2].

**Table 4.** Thermal and photo degradation rate constants.

| Ageing condition | Rate constant, k ($d^{-1}$) | Rate constant, k ($d^{-1}$) |
|---|---|---|
| Thermally ageing | ATO-HBCD | ATO-DBE 209 |
| 298.15 K | $7.59\times10^{-3}\pm8\times10^{-4}$ | $9.20\times10^{-3}\pm8\times10^{-4}$ |
| 333.15 K | $1.89\times10^{-2}\pm2\times10^{-4}$ | $2.14\times10^{-2}\pm2\times10^{-4}$ |
| 363.15 K | $4.80\times10^{-2}\pm4\times10^{-3}$ | $4.10\times10^{-2}\pm7\times10^{-3}$ |
| UV aged sample | $3.40\times10^{-2}\pm4\times10^{-3}$ | $3.83\times10^{-2}\pm4\times10^{-3}$ |

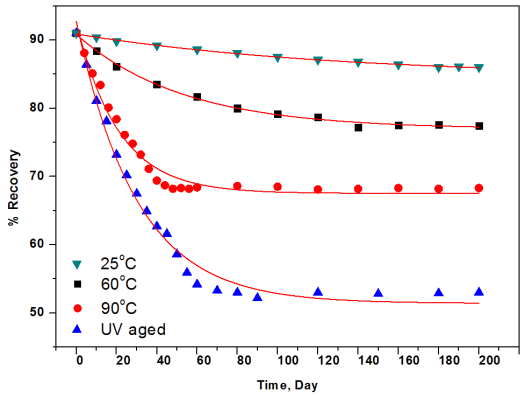


**Figure 1.** Time-dependence of the release of antimony trioxide upon thermal and UV exposure from ATO-HBCD samples.

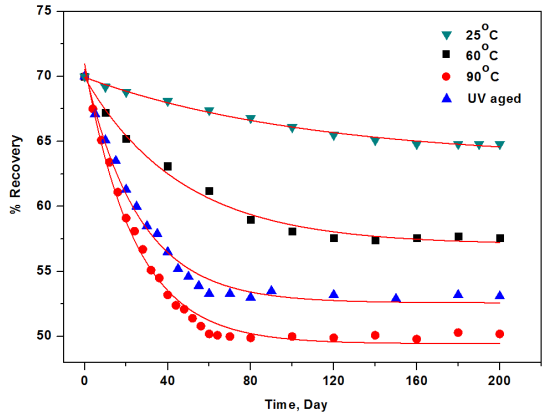


**Figure 2.** Time-dependence of the release of antimony trioxide upon thermal and UV exposure from ATO-HBCD samples.

In general, for both textile samples, the release rate of type B is faster than type A samples under thermal and UV- aged conditions ( exception could be observed for the release rat at 90 °C were both results are comparable). However, the release rate ratio of higher temperature compared to lower one for type A ( ATO-HBCD) is higher compared to type B (ATO-BDE 209) [2].

For type A textile samples: the release rate of ATO at 90 °C is 2.1 times faster compared to release rate at 60 °C and is five times faster compared to release rate at 25 °C [1,2]. On the other hand, for type B samples; the release rate of ATO at 90 °C is 1.5 times faster compared to release rate at 60 °C and is 3.5 times faster compared to release rate at 25 °C. Direct comparison of the rate constants of the thermally aged samples with that of the UV aged samples indicates that the release of antimony trioxide from the back-coated textile was also enhanced by UV exposure. Taking into account the ageing period used in this study, we can conclude that the exposure of textile samples to UV light enhances the release of antimony trioxide more effectively than when exposed to thermal ageing. The release rate of type B is faster compared to type A [1,2].

In comparison to UV effect on the leach of HBCD and DBE 209 from backcoated textile we report that exposure of the textile samples to the UVA light not only accelerate the leach of the BDE 209 from the textile samples but also accelerate the photodecomposition of the BDE 208 into lower congeners while exposure of the HBCD textile samples to UVA affect the leach rate only and no photo products were detected other than the isomers of HBCD [1,2].

The systematic influence of temperature on the rate constants ($k_{obs}$) was also studied and experimental data were fitted according to Eyring equation (Equation (2)) [1,2] from which the enthalpy of activation were estimated to be $\Delta H^{\neq}$ = 19.9±0.1 and 14.6 kJ/mol for type A and type B, respectively, and the entropy of activation $\Delta S^{\neq}$ were -219±0.4 and -234±0.5 J/mol for type A and type B, respectively. Low value of $\Delta H^{\neq}$ and the negative $\Delta S$ indicates that the ATO is not covalently bound to the polymer textile as expected and can easily leach from the back-coated textile. Comparison of the activation parameters of type A with type B textile samples indicates that ATO seem to be more bounded with BDE 209 compared to HBCD textile samples which also explain the more percentage release from type A samples compared to type B.

### *3.4. Migration of ATO into biological fluids*

Leaching of ATO from the back-coated textile could result in a large scale risks to human health [1,2]. Leached antimony trioxide could be absorbed by human body according one of the following two scenarios [1]. The first scenario is based on the direct contact between the textile and the skin which could be studied through the contact-blotting extraction method [1,2], and the other one is by oral exposure related to repeat sucking of back-coated textile Which could be studied through the Head-over-heels method [1,2]. The presence of biological fluid was found to enhance the release of the FR from the textile material [2] and therefore increase the risk of its absorption by the human body, therefore, both skin and oral exposure were studied under the effect of different artificial biological fluids [1,2] (to simulate the effect of biological fluid on the migration of antimony trioxide from the back-coated textile in presence of biological fluid); water, artificial saliva, artificial perspiration and 5% citric acid (chosen to simulate acid, food, or beverages, orange juice). Migration of ATO into the biological fluid was studied for both unaged and thermally and UV aged samples [1,2].

Table 5 reports the total amount of ATO migrated from the back-coated textile into the extraction fluid following the Head-over-Heels test for the unaged, thermally aged and UV exposed samples. In general, more ATO is released for the UV-aged materials compared to the thermally aged or unaged materials. On the other hand, for the thermally aged textile samples less amount of ATO were released from the thermally aged samples (2 to 4 times less ATO released from aged fabrics in comparison with unaged materials). These results suggest that the ageing loss and extractible loss of the brominated FRs and antimony trioxide in the Head-over-Heels test are not coupled and behave independently ( i.e., we already reported that the migration of BDE 209 or HBCD into the biological fluid is significantly increased for samples previously exposed to UV radiation or aged under different conditions) [2,25].

**Table 5.** Results of the Head-over-Heels test for the textile fabric from samples.

| Extraction medium | Sample | Un-aged | UV-aged | Thermally aged | | |
|---|---|---|---|---|---|---|
| | | | | 25 °C | 60 °C | 90 °C |
| | | Recovery (%) [2,3] | Recovery (%) [2,3] | Recovery (%) [2,3] | Recovery (%) [2,3] | Recovery (%) [2,3] |
| Distilled water | Blank | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| | ATO-HBCD [1] | 0.81±0.02 | 1.20±0.04 | 0.90±0.01 | 0.64±0.04 | 0.24±0.04 |
| | ATO-DBE 209 [1] | 0.75±0.04 | 1.14±0.07 | 0.73±0.03 | 0.53±0.03 | 0.17±0.02 |
| Artificial [4] saliva | Blank | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| | ATO-HBCD [1] | 1.08±0.01 | 1.65± 0.02 | 0.85±0.04 | 0.72±0.02 | 0.66±009 |
| | ATO-DBE 209 [1] | 0.72±0.08 | 1.62±0.02 | 0.54±0.03 | 0.45±00.2 | 0.34±0.05 |
| Citric acid [4] | Blank | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| | ATO-HBCD [1] | 1.1±0.1 | 1.25±0.05 | 0.81±0.01 | 0.62±0.04 | 0.42±0.08 |
| | ATO-DBE 209 [1] | 0.89±0.03 | 1.23±0.01 | 0.65±0.03 | 0.42±0.02 | 0.27±0.09 |
| Artificial sweat | Blank | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| | ATO-HBCD [1] | 1.20±0.02 | 1.85±0.04 | 0.91±0.02 | 0.54±0.03 | 0.34±0.04 |
| | ATO-DBE 209 [1] | 0.86±0.02 | 1.75±0.01 | 0.62±0.03 | 0.42±0.01 | 0.21±0.02 |

[1] Fabric samples of type A (HBCD/ATO) and Type B(ATO/DBPE) contain 3.6 and 4.3% by weight, respectively.
[2] Percentage of $ATO_3$ recovered compared to theoretical concentration of ATO contained on the fabric sample.
[3] Results are average of thee sample.
[4] Small concentration of antimony detected in the blank samples, analysis of control samples of citric acid and artificial saliva suggest that the citric acid and saliva contain a background of antimony from the reagent used to make the solutions therefore; the recovered results are corrected for the background results.

**Table 6.** Results of the Contact blotting test for the textile fabric from samples.

| Extraction medium | Sample | Un-aged | UV-aged | Thermally aged | | |
|---|---|---|---|---|---|---|
| | | | | 25 °C | 60 °C | 90 °C |
| | | Recovery (%) [2,3] | Recovery (%) [2,3] | Recovery (%) [2,3] | Recovery (%) [2,3] | Recovery (%) [2,3] |
| Distilled water | Blank | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| | ATO-HBCD [1] | $(1.3\pm0.2)\times10^{-4}$ | $(8.9\pm0.1)\times10^{-4}$ | $(1.2\pm0.2)\times10^{-4}$ | $(3.7\pm0.8)\times10^{-4}$ | $(6.3\pm0.5)\times10^{-4}$ |
| | ATO-DBE 209 [1] | $(6.6\pm0.4)\times10^{-4}$ | $(1.1\pm0.3)\times10^{-3}$ | $(9.0\pm0.5)\times10^{-4}$ | $(1.0\pm0.9)\times10^{-3}$ | $(1.2\pm0.6)\times10^{-3}$ |
| Artificial [4] saliva | Blank | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| | ATO-HBCD [1] | $(1.5\pm0.3)\times10^{-3}$ | $(4.9\pm0.7)\times10^{-3}$ | $(2.1\pm0.3)\times10^{-3}$ | $(3.8\pm0.2)\times10^{-3}$ | $(4.8\pm0.5)\times10^{-3}$ |
| | ATO-DBE 209 [1] | $(7.5\pm0.3)\times10^{-4}$ | $(1.7\pm0.5)\times10^{-3}$ | $(0.91\pm0.02)\times10^{-3}$ | $(1.3\pm0.3)\times10^{-3}$ | $(1.8\pm0.8)\times10^{-3}$ |
| Citric acid [4] | Blank | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| | ATO-HBCD [1] | $(1.4\pm0.1)\times10^{-3}$ | $(2.6\pm0.2)\times10^{-3}$ | $(1.9\pm0.5)\times10^{-3}$ | $(2.1\pm0.5)\times10^{-3}$ | $(2.5\pm0.9)\times10^{-3}$ |
| | ATO-DBE 209 [1] | $(1.1\pm0.2)\times10^{-3}$ | $(4.7\pm0.5)\times10^{-3}$ | $(1.8\pm0.3)\times10^{-3}$ | $(3.2\pm0.3)\times10^{-3}$ | $(4.9\pm0.2)\times10^{-3}$ |
| Artificial sweat | Blank | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| | ATO-HBCD [1] | $(3.1\pm0.3)\times10^{-3}$ | $(8.7\pm0.8)\times10^{-3}$ | $(3.7\pm0.1)\times10^{-3}$ | $(5.9\pm0.8)\times10^{-3}$ | $(9.7\pm0.5)\times10^{-3}$ |
| | ATO-DBE 209 [1] | $(2.4\pm0.4)\times10^{-3}$ | $(7.3\pm0.2)\times10^{-3}$ | $(4.1\pm0.4)\times10^{-3}$ | $(6.2\pm0.4)\times10^{-3}$ | $(8.2\pm0.8)\times10^{-3}$ |

[1] Fabric samples of type A (HBCD/ATO) and Type B (ATO/DBPE) contain 3.6 and 4.3% by weight, respectively.
[2] Percentage of ATO recovered compared to theoretical concentration of ATO contained on the fabric sample.
[3] Results are average of thee sample.
[4] Small concentration of antimony detected in the blank samples, analysis of control samples of citric acid and artificial saliva suggest that the citric acid and saliva contain a background of antimony from the reagent used to make the solutions therefore, the recovered results are corrected for the background results.

At this point, it is important to highlight the following points regarding the migration of ATO into the biological fluid [2]:

1) The migration of ATO into the biological fluid was observed for both samples types (ATO-HBCD and ATO DBD 209) regardless if it is thermally/ UV aged or not.
2) More ATO release was reported for type A textile samples compared to type B samples.
3) ~81% *wt*:*wt* of the total amount of ATO present in the back-coated textile type A was found to leach into water from the un-aged backcoated textile compared to 0.75 %. *wt*:*wt* of the total amount of ATO leached in case of type B ( both of them are comparable).
4) The presence of biological fluids enhances the migration of ATO from the un-aged back-coated textile compared to water by 40 and 9% from type A and type B, respectively.
5) For the thermally aged samples, the amount of ATO migrating into the biological fluid was strongly affected by the aging temperature. It seem that ATO leach from the backcoated textile during the ageing process As ageing temperature increased, less amount of ATO migrate into the biological fluid.
6) ATO became eventually less tightly bound to the polymer textile under the condition of UV exposure, therefore it can easily leach from the textile exposed to UV, again, the presence of biological fluids was found to increase the migration of ATO from the back-coated textile compared to water [1,2,25].

Exposure of (FR) containing textiles to skin was simulated by the contact blotting test. Table 6 reports the total amount of ATO migrated from the back-coated textile into the filter paper in contact blotting test for the unaged, thermally aged and UV exposed samples. In general, migration of ATO from textile into filter papers were observed for all samples, this result is interesting since it was reported that neither DBE 209 nor HBCD was transferred to the filter paper [1,2,25]. Results of contact blotting test could be summarized as follow:

1) For unaged samples, more ATO released from Type A samples compared to Type B samples in presence of biological fluid.
2) Migration of ATO occurs at very low levels, however, presence of biological fluids enhance the migration rate (i.e., up to 24 times more ATO being transferred for the artificial sweat in comparison to distilled water in Type A).
3) ATO became eventually less tightly bound to the polymer textile under condition of UV exposure, therefore it can easily leach from the textile exposed to UV, and again, the presence of biological fluids was found to increase the migration of ATO rate (i.e., the recovery of ATO is increased by factor up to 7 from the UV aged samples).
4) For the thermally aged samples, the amount of ATO migrating into the biological fluid was strongly affected by the aging temperature. As ageing temperature increased, more amount of ATO migrates into the biological fluid, which implies that ATO leached from the textile during the ageing process.

## 4. Conclusions

In this work, the kinetics of the thermal and photolytic release of ATO from back-coated textiles was studied for two types of textile samples type A (ATO-HBCD) and Type B (ATO-BDE 209)) [1,2]. In general, the segregation of ATO from thermally and UV aged samples was found to follow the first order kinetics with rate constants increasing directly related to ageing temperature. Exposure of the textile samples to UV radiation also increases the rate of ATO release from the back-coated textile with rate constant comparable to the thermally aged samples. Leaching of ATO was observed in both aged and unaged textile samples. ~0.81% *wt*:*wt* of the total amount of ATO present in the back-coated textile type A was found to leach into water from the un-aged backcoated textile compared to 0.75%. *Wt*:*wt* of the total amount of ATO leached in case of type B. The presence of biological fluids enhances the migration of ATO from the un-aged back-coated textile compared to water by 40 and 10% from Type A and Type B, respectively. Ageing temperature strongly affect leaching of ATO from the backcoated textile therefore, ATO leach from the backcoated textile during the ageing process As ageing temperature increased, less amount of ATO migrate into the biological fluid.

Simulation of the direct contact between the textile and the skin using the contact blotting test revealed that ATO migrate from the backcoated textile into the filter paper for both samples type under different conditions; biological fluids were found to enhance the migration of ATO [1,2].

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