

STUDY OF THERMAL BEHAVIOUR OF SOME DERIVATIVES OF  
TRIPHENYLAMINE, WITH A VIEW TO OBTAINING NEW  
STATIONARY PHASES FOR GAS CHROMATOGRAPHY

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A study was carried out upon the thermal behaviour of eight derivatives of triphenylamine, i. e. trinitrotriphenylamine; triaminotriphenylamine; triaminotriphenylamine chlorhydrate, tetraphenylborate and picrate; and a trisazo derivative and its compound with Be(II) and U(VI). The aim of this study was to find compounds with satisfactory thermal stability for use as stationary phases in gas chromatography.

Triaminotriphenylamine was previously used as an indicator for the argentometric determination of halide ions and as a reagent for the spectrophotometric determination of Ag(I) [1]. Triaminotriphenylamine chlorhydrate was used as a reagent for the spectrophotometric determination of SO<sub>2</sub> and NO<sub>2</sub> in the atmosphere [2].

In view of the excellent analytical behaviour of these compounds, we have carried out a thermal investigation of some derivatives of triphenylamine, i.e. trinitrotriphenylamine (a synthesis intermediate), a compound synthesized by us following a method advanced by Walter [3]; triaminotriphenylamine, which was synthesized by a method proposed by Neunhoeffer [4]; triaminotriphenylamine chlorhydrate [4]; triaminotriphenylamine tetraphenylborate; and triaminotriphenylamine picrate. The latter two were synthesized by us by coupling triaminotriphenylamine chlorhydrate with sodium tetraphenylborate and picric acid, respectively.

We also considered the thermal behaviour of trisazo reagent of triphenylamine, resulting from coupling with salicylic acid. This reagent was used by us for spectrophotometric determination of U(VI) [5] and Be(II) [6]. Since we were able to obtain the Be(II) and U(VI) compounds in the solid state, the thermal behaviour of these compounds was also investigated.

The ultimate aim of this study was to characterize the above-mentioned compounds and, at the same time, to search for new, thermally stable compound which could possibly be used as stationary phases in gas chromatography.

### Experimental

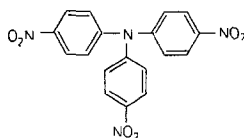
A derivatograph was used to determine the thermal behaviour of the investigated compounds. The experimental parameters of the instrument were as follows:

Heating rate of the furnace: 5°/min, except for the trisazo derivative for which the rate was 2.5°/min.

The temperature and the differential temperature were measured with Pt/Pt-Rh thermocouples. A static, environmental atmosphere in the furnace. Amount of sample investigated:  $0.15 \pm 0.02$  g.

### Results and discussion

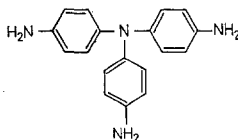
#### *Trinitrotriphenylamine (TNTPA)*



(Formula A)

The thermal curves (Fig. 1a) show that the compound is thermally stable up to about 260°, at which point a small mass loss occurs in the compound. Explosive decomposition of the compound takes place at 340°, whereas the maximum thermal effect was observed at about 300°. Above this temperature, pyrolysis begins of the compound remaining after departure of NO<sub>2</sub>.

#### *Triaminotriphenylamine (free base, TATPA):*



(Formula B)

The free base is thermally stable up to 230°; above this temperature, a slight thermal decomposition begins, which can be seen in the thermal curves as an endothermic effect, whose peak is located at 350°. At 215°, the DTA curve shows a small exo-endothermic effect, which can be assigned to a physical phenomenon, possibly a polymorphic modification or melting of the compound (Fig. 1b).

#### *Triaminotriphenylamine chlorhydrate*

This compound is thermally unstable. A slight decomposition occurs at room temperature and becomes more marked as the temperature increases. The TG curve does not have a horizontal portion over the temperature range investigated (Fig. 1c).

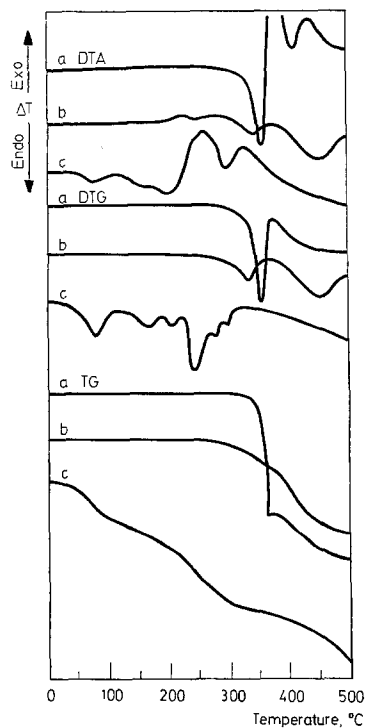


Fig. 1. The thermal curves obtained at a heating rate of  $5^{\circ}/\text{min}$  up to  $500^{\circ}\text{C}$  for (a) trinitrotriphenylamine; (b) triaminotriphenylamine (free base); and (c) triaminotriphenylamine chlorhydrate

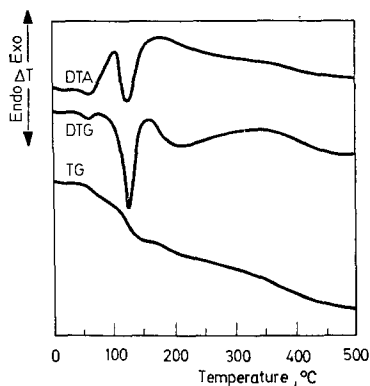


Fig. 2. The thermal curves of triaminotriphenylamine tetraphenylborate at a heating rate of  $5^{\circ}/\text{min}$

#### *Triaminotriphenylamine tetraphenylborate*

This compound displays a slight mass loss, starting from room temperature and continuing up to  $75^{\circ}$ , where a pronounced decomposition sets in, accompanied by mass loss (Fig. 2).

*Triaminotriphenylamine picrate*

The mass loss observed for this compound up to 110° (Fig. 3) is due to moisture. Afterwards the compound is thermally stable up to 150°, above which point thermal decomposition occurs, with a pronounced explosive character.

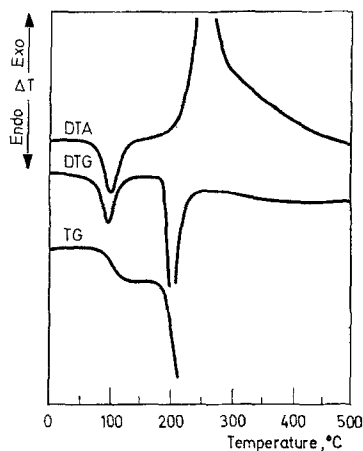
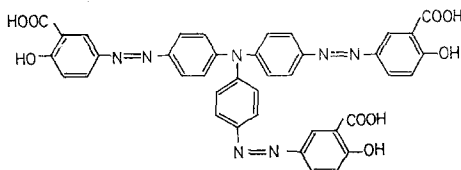


Fig. 3. The thermal curves of triaminotriphenylamine picrate at a heating rate of 5°/min

*The trisazo derivative of triaminotriphenylamine*

(Formula C)

For this compound, a mass loss of about 10% was observed in the interval 50–110° (Fig. 4a), after which the compound is stable up to 230°. At this temperature, a specific, self-ignition thermal effect occurs (Fig. 4, the curves obtained for a heating rate of 5°/min). After this effect is over, the thermal curves show a continual mass loss, until the compound is completely carbonized.

We repeated the analysis of this compound by heating it up to 225°. Within this range, it had a moisture-like mass loss of 10.5% at 50–110°. If the compound is cooled down and then reheated it exhibits good thermal stability (Fig. 4b).

*The compound of the trisazo compound with Be(II)*

The thermal behaviour of this compound of beryllium is similar to that of the trisazo compound itself. It also has a mass loss in the range 50–110°; thereafter

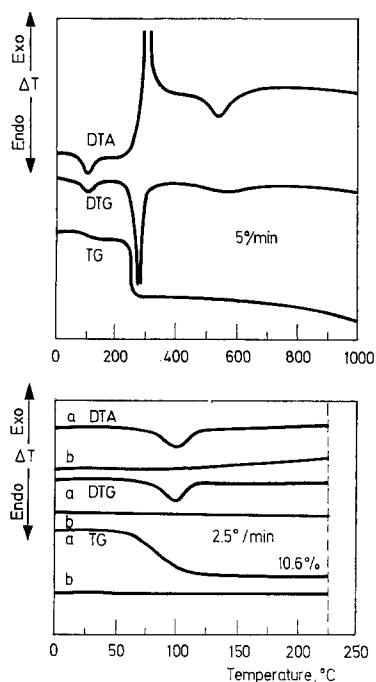


Fig. 4. The thermal curves of the trisazo derivative of triaminotriphenylamine, obtained at two heating rates: (a) the compound heated up to 250°C; (b) thermally reanalyzed after heating to 250°C and cooling

the compound is stable up to about 230°, at which point thermal decomposition sets in (Fig. 5a). It is worthwhile mentioning that, after heating at 1000°, virtually no residue was obtained for the reagent (the mass loss being 99.74%), whereas the total mass loss for the beryllium compound was only 96.84%.

#### *The compound of the trisazo compound with U(VI)*

The thermal behaviour of this compound is somewhat different from that of the reagent. Even though it starts with a moisture-like mass loss, its decomposition temperature is higher than that of the reagent, at about 300°, and the total mass loss up to 1000° is only 62.16% (Fig. 5b).

### Conclusions

Since the aim of this study was merely to ascertain the thermal stabilities of the compounds, no attempts were made to interpret the thermal curves quantitatively. On the basis of our study we consider that triaminotriphenylamine (free base, TATPA) and the trisazo derivative of triaminotriphenylamine can be used under good conditions as stationary phases in gas chromatography.

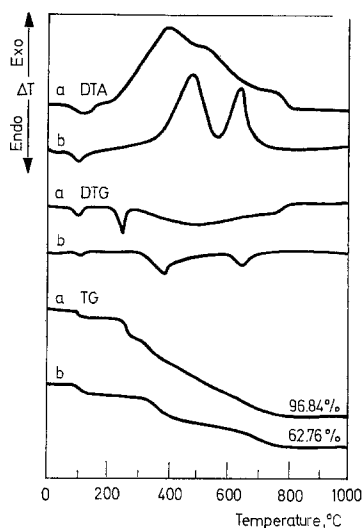


Fig. 5. The thermal curves of the complexes of Be(II) and U(VI) with the trisazo derivative: (a) the Be(II) complex; (b) the U(VI) complex

### References

1. M. E. M. KHALIFA, paper submitted to *Talanta*.
2. M. E. M. KHALIFA, C. GREFF and G. E. BAULESCU, *Anal. Lett.*, 14 (1981) 249.
3. R. I. WALTER, *J. Amer. Chem. Soc.*, 75 (1953) 2771.
4. O. NEUNHOEFFER and P. HEITMANN, *Chem. Ber.*, 92 (1959) 245.
5. M. E. M. KHALIFA, C. GREFF and G. E. BAULESCU, *Revista de Chimie (Bucharest)*, 32 (1982) 474.
6. M. E. M. KHALIFA, *Analyst (London)*, 107 (1982) 446.

**ZUSAMMENFASSUNG** — Eine umfassende Untersuchung zum thermischen Verhalten von acht Triphenylaminderivaten, d. h. Trinitrotriphenylamin, Triaminotriphenylamin, Triaminotriphenylamin Chlorhydrat, Tetraphenylborat und Pikrat, sowie ein Trisazoderivat und seine Verbindungen mit Be(II) und U(VI) wurde durchgeführt. Der Zweck dieser Studie war Verbindungen befriedigender Thermostabilität zum Einsatz als stationäre Phasen in der Gaschromatographie zu finden.

**Резюме** — Проведено исследование термического поведения восьми производных трифениламина: тринитротрифениламина, триаминотрифениламина, солянокислой соли-, тетрафенилбората- и пикрата триаминотрифениламина, трисазопроизводного триаминотрифениламина и его соединений с Be(II) и U(VI). Целью исследования являлось найти соединения с удовлетворительной термоустойчивостью для использования их в качестве неподвижных фаз в газовой хроматографии.