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Why wrong data on triphosgene stability circulated. Perception and Cognition, an addition to a previous article (1a)

Crystalline triphosgene has been established during the last twenty years in a steady market as a commonly used equivalent to substitute the gaseous poison phosgene (1) in small scale applications. Using solid triphosgene (which is also a poison) crucial is thermal stability. Recent reliable and precise analysis in 2011 (1a) has resulted in its thermal decomposition at 201-204°C. This is in good accordance with early data on it in 1929 (2). Since 1996 (1d) various and rather arbitrary values of 130-170°C stumbled through the internet, which have been corrected, when found. Even a triphosgene producer gave a value of 160°C (3). Since thermal stability is the key date for a safe triphosgene usage, sense of responsibility charges to investigate these wrong data.

To find out, why some analysts published wrong data, we checked up how latter could be obtained and interpreted. Generally when carrying out a DSC (differential scan calorimeter) measuring, crucibles of aluminium are commonly used. Thus we used an alu (instead of glass) crucible for the triphosgene DSC measuring. These experiments had run completely different to those in crucibles of glass (1a). The data can directly be seen in Figure 1 and Figure 3.

Under pressurization conditions (Figure 1), the crucible was hermetically closed, traces of phosgene and the triphosgene reacted with the aluminium metal of the crucible to form aluminium chloride AlCl_3 and carbon monoxide CO , which is a

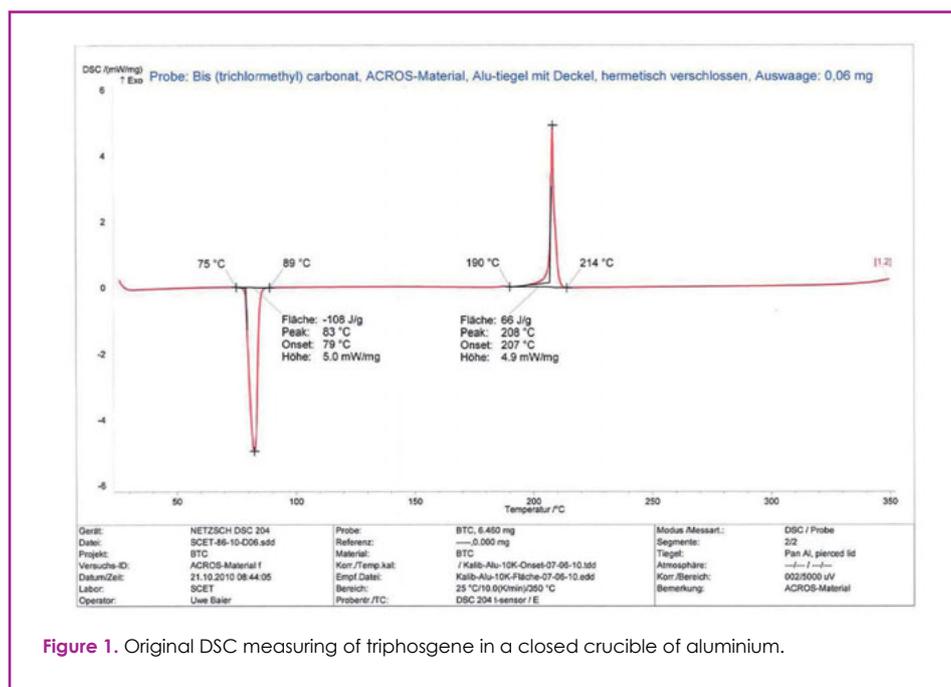


Figure 1. Original DSC measuring of triphosgene in a closed crucible of aluminium.

well-known exothermic reaction (4) (Figure 2). Generated AlCl_3 catalysed the decomposition of triphosgene to form carbon dioxide, tetrachloro methane, and phosgene (1b), which reacted onward with aluminium, and so on. Reaction enthalpy is -66 J g^{-1} .



Figure 2. Reaction of phosgene with Al metal to form AlCl_3 .

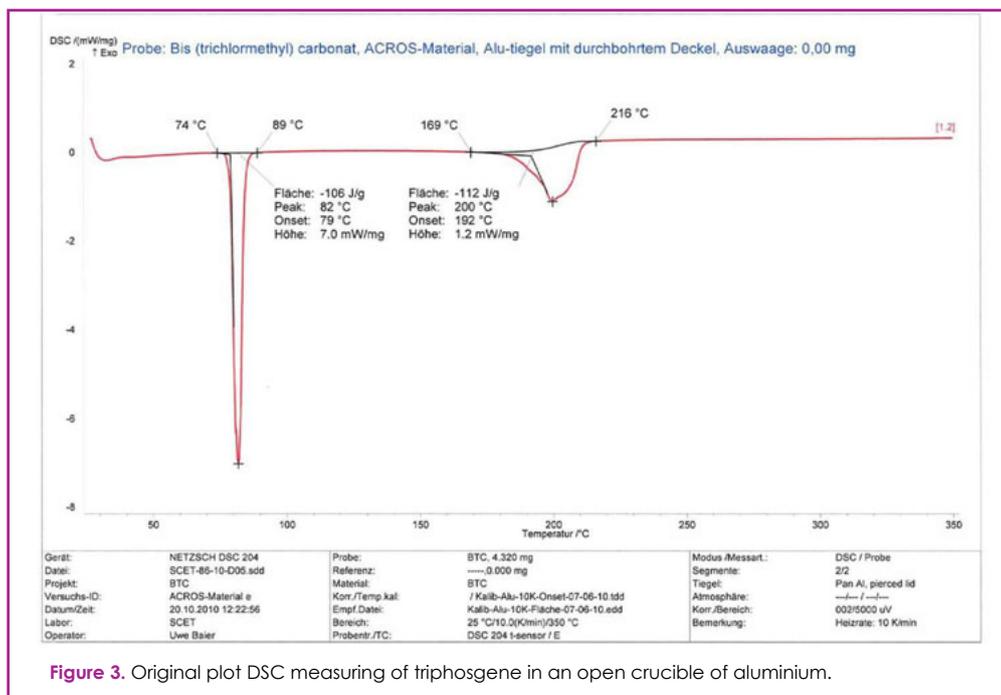


Figure 3. Original plot DSC measuring of triphosgene in an open crucible of aluminium.

Figure 3 shows an endothermic reaction of triphosgene in an open crucible with an onset at 169°C and a reaction enthalpy of +112 J g⁻¹. This behaviour could be interpreted by the decomposition of solid triphosgene into gaseous products carbon dioxide, tetrachloro methane, and phosgene (1b), which immediately escaped the perforated crucible and thus outbalanced the negative decomposition enthalpy by the endothermic evaporation enthalpy of decomposition products (calculated to +240 J g⁻¹). The decomposition reaction had been catalyzed by generated traces of aluminium chloride (see above).

CONCLUSION

Our above data using aluminium crucibles are similar to the wrong data on triphosgene thermal stability (1d, 3). Thus it can be assumed that in some published former DSC measurements of triphosgene the standard method using aluminium crucibles had been applied. This would explain the completely different course of triphosgene *chemical potential* in the chemical reaction with aluminium instead of only the phase transition. The analysts followed merely the *perception* of measurement data for an *expected* reaction. What fails, was the right interpretation by an experienced chemist, who would have known the reaction of phosgene/triphosgene with aluminium, and thus got the *cognition* about what really had happened in DSC runs.

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