

## The Ryan-Gourley-Jones Paper from August 2008

Here are some comments on the new paper in *The Environmentalist* by K. Ryan, J. Gourley and S. Jones (RGJ) entitled "Environmental Anomalies at the World Trade Center: Evidence for Energetic Materials"

The main topic of discussion in the RGJ paper is the very high levels of volatile organic compounds (VOCs) such as benzene that were detected in the air at or near Ground Zero for up to 6 months after the September 11<sup>th</sup>, 2001 attacks on the WTC. Thus, using data reported by the US EPA, RGJ present plots of the daily maximum concentrations of benzene, toluene, ethylbenzene, and styrene over the period September to November 2001 and note that these data show sharp peaks in the concentrations of these VOCs on certain days while remaining at relatively low concentrations at all other times. RGJ acknowledge that these VOCs are among the expected products of the combustion of common plastics such as PVC and polystyrene, but question the causes of the extreme spikes in their concentrations.

It would appear reasonable to assume that clean-up operations occasionally stimulated fires in localized areas of the rubble pile leading to acute releases of combustion gases from burning/smoldering plastic materials in the pile. However, RGJ point out that other less well-known VOCs such as propylene, 1,3-butadiene and 1,3-diphenylpropane (1,3-DPP) appear to be associated with the benzene, toluene, ethylbenzene, and styrene acute releases. RGJ go on to suggest that the detection of one VOC in particular, namely 1,3-DPP, is evidence for the presence of the pyrotechnic agent: sol-gel "nanocomposite" thermite. Now Steven Jones first mentioned this idea about two years ago, prompting me to make the following post on the PhysOrg forum on July 22, 2006:

"I AM a chemist, and I once worked under contract to ICI in the UK on the thermal degradation of polymers....

Thermal degradation of PVC yields mainly benzene, toluene, xylene, ethylbenzene, and various chlorobenzenes.

All of these species were detected by the EPA in air samples taken at various locations in NYC after 9-11.

Thermal degradation of POLYSTYRENE yields styrene, alpha-methylstyrene and 1,3-diphenylpropane.

The EPA website on air-sampling at NYC includes data for styrene, but curiously does NOT list data for 1,3-diphenylpropane. (However, I believe this may be simply because this compound is not on the EPA's "priority pollutant" list)

NIST and others have noted that TONS of PLASTICS burned in the Twin Towers and the rubble pile during and long after 9-11.

Polystyrene was surely one of those plastics! (By the way, the quote about 1,3-diphenylpropane being associated with PVC appears to be in error. I suspect the person meant polystyrene!)

So I would say that Prof. Jones, once again, has found something in a sample from the WTC site that can be explained WITHOUT INVOKING thermite/thermate."

<http://www.physforum.com/index.php?showtopic=7444&st=660>

Let's therefore consider the relative merits of the RGJ hypothesis for the origin of 1,3-DPP in the air above Ground Zero as compared to the alternative view that 1,3-DPP is simply an expected thermal decomposition product of the common plastic polystyrene. To begin the discussion, consider this paragraph from page 9 of the RGJ paper:

*“Other studies have shown trace amounts of 1,3-DPP as a secondary product of polystyrene combustion or thermolysis. But such studies suggest that 1,3-DPP may only form in negligible quantities and under certain conditions (Boettner et al. (1973); McCaffrey et al. (1996)). In such experiments, the major product of the combustion or thermolysis of polystyrene, far outweighing others, is the monomer styrene. This leads us to the fact that, although styrene was a species of interest at 290 Broadway during the same time period as was 1,3-DPP, styrene detections were not reported in the FOIA provided data (EPA (2004)). Therefore, it appears that Swartz' first suggested hypothesis, that 1,3-DPP resulted from combustion of polystyrene, is not probable.”*

This paragraph, while somewhat confusing, is actually quite deceptive in view of what it implies:

- (i) That negligible amounts of 1,3-DPP are formed during the combustion or thermolysis of polystyrene.
- (ii) That the EPA did not detect styrene in the air at or near Ground Zero after 9/11.

Now both of these claims are untrue as other data, including some presented in the RGJ paper itself, amply demonstrate. Thus, Table 1 of the RGJ paper provides examples of EPA data for styrene in the air at Ground Zero including a value of 180,000 ppb reported for October 11<sup>th</sup> 2001, - a level that was about three times higher than the concentration of benzene for that day. However, and here we reveal another problem with the RGJ paper, it is important to note that the 180,000 ppb concentration for styrene is a peak value obtained from a grab sample collected at Ground Zero on the date in question.

The issue of the sampling locations and techniques used to measure VOCs at the WTC site after 9/11 is addressed in the EPA *Summary Report EPA/600/R-03/142*, published in 2003. Thus on page 30 of this report we read:

*“Most of the VOC data are from grab samples, which were not collected to characterize exposures but were intended to inform recovery workers within the restricted zone of the location of hot spots. As a result, the locations for most of the sampling were near the sources and plumes of smoldering fires, ..... Although grab samples of VOCs can be valuable for indicating high levels at certain locations and give an indication of which chemicals are present, 24-hour samples would be much more appropriate for exposure assessment.”*

Full day air samples were in fact collected by the EPA at eight sites along the outer edges of the rubble pile and confirm that average levels were much lower than many of the

levels captured in grab samples which were collected “near smoldering fires” within the rubble pile over time intervals lasting “but a few minutes”.

Thus in order to make useful comparisons to published data on 1,3-DPP at the WTC we need to consider where and how the sampling for VOCs was carried out – an issue not addressed in the RGJ paper. If we read Swartz’ paper, (See: *Environmental Science and Technology* 37, 3537, (2003)), we find that his sampler, which was located about ½ km from the WTC at 290 Broadway, operated for 11.5 to 23 hours and collected ~ 0.6 micrograms of 1,3-DPP per cubic meter of air, ( $0.6 \mu\text{g}/\text{m}^3$ ), between October 4<sup>th</sup> and 21<sup>st</sup> 2001. Now, regrettably, Swartz does *not* report data for styrene since the emphasis of his research was polycyclic aromatic hydrocarbons (PAHs). However, there *are* post-9/11 airborne styrene concentrations reported at locations close to the perimeter of the WTC site by other researchers. For example, Olsen et al, (See: *Atmospheric Environment* 41, 5673, (2007)), report an average styrene concentration of about  $2 \mu\text{g}/\text{m}^3$  at a site just north of the WTC between September 2001 and January 2002. Also Geyh et al. (See: *Journal of Occupational and Environmental Hygiene*, 2 179 (2005)), report that the styrene concentration was about  $5 \mu\text{g}/\text{m}^3$  at a number of sites at the perimeter of the WTC complex in October 2001.

Based on these data it would appear reasonable to say that in mid October 2001 the concentration of 1,3-DPP was about 20 % of the styrene concentration at the perimeter of the WTC rubble pile. And this brings us to the other point of dispute with the RGJ paper, namely the possibility that 1,3-DPP in the air at Ground Zero was produced by the thermal decomposition of polystyrene. Now the RGJ paper asserts that for polystyrene under conditions of combustion or thermolysis: “*1,3-DPP may only form in negligible quantities.*” However, only two references are cited to support this claim: a 1973 study of the combustion of a wide variety of plastics and a 1996 study of the thermolysis of a mixture of polystyrene and polyethylene. While it is acknowledged that these particular studies may indeed have failed to detect significant quantities of 1,3-DPP, it is worth asking if there are situations that could enhance the production of 1,3-DPP during the thermal decomposition of polystyrene.

A survey of the published literature on the pyrolysis of polystyrene reveals that the decomposition of polystyrene is a complex process that depends on a number of factors including the time and temperature profile of the pyrolysis experiment and the nature of the starting material. Potsuma, (See *Polymer Degradation and Stability* 91, 2979, (2006)), has shown that the pyrolysis of polystyrene yields measurable amounts of styrene, alpha-methylstyrene, ethylbenzene, cumene, 2,4-diphenyl-1-butene, toluene, 1,3,5-triphenylpentane, 2,4,6-triphenyl-1-hexene and 1,3-diphenylpropane (1,3-DPP). However, the composition of the mixture changes significantly with the amount of product formed and the temperature. In general, very little 1,3-DPP is formed during the initial stages of the decomposition reaction, but as the degree of decomposition increases, more 1,3-DPP is formed at the expense of toluene. Complete reaction at ~ 300 °C yields 39 wt% styrene and 9 wt % 1,3-DPP implying a 1,3-DPP/styrene ratio of about 1:4.

The chemistry of the thermal decomposition of polystyrene becomes even more complex when “real-world” plastics are involved. First it should be noted that because pure polystyrene is quite brittle and softens near 100 °C, additives are incorporated into commercial polystyrene to achieve improved material properties that are required for the intended end usage. Additives include organic and inorganic compounds and are used as cross-linking agents, plasticizers, fillers/pigments, heat stabilizers, antioxidants, uv stabilizers, impact modifiers, processing lubricants, anti-static agents, flame retardants, etc, (See *Chromatographia*, 56 (3/4), 165, (2002)). Valavanidis et al. (See *Journal of Hazardous Materials* 156, 277, (2008)), have collected particulate material from the combustion of plastics such as polystyrene, polyvinyl-chloride and polyethylene and found that samples decomposed at ~ 700 °C left residues containing Na, Ca, Al, Si, Fe, Zn, Ba, Pb, etc, that constituted up to 10 wt % of the starting material.

Another consideration in discussing the pyrolysis of commercial polystyrene is the fact that, apart from the well-known material Styrofoam, polystyrene is generally used in polymer blends - two popular examples being ABS and HIPS. ABS is an acrylonitrile-butadiene-styrene polymer while HIPS is high-impact polystyrene, an impact resistant material made from a styrene-butadiene grafted blend. ABS and HIPS are commonly used in TV housings and computer equipment and are reported to account for more than 50 % of the waste plastics found in discarded electric and electronic equipment.

Two studies of the pyrolysis of mixed plastics used in commercial electrical and electronic products are pertinent to the present discussion. In one study, Day et al., (See *Journal of Analytical and Applied Pyrolysis* 52, 199, (1999)), pyrolysed ABS alone and mixed with other plastics such as PVC or electrical components such as metallic copper at temperatures in the range 700 – 900 °C. ABS by itself released many organic species that included 1,3 butadiene, 1,3-diphenylpropane and styrene with the 1,3-DPP being about 3 % relative to the styrene – a concentration ratio expected for such high pyrolysis temperatures. However, pyrolysis of ABS in the same high temperature range in the presence of PVC and metallic copper increased the 1,3-DPP yield to about 6 % relative to styrene, illustrating the promoting effects of PVC and/or copper on the release of 1,3-DPP from polystyrene blended plastics.

In the other study noted above, Bhaskar et al. investigated the pyrolysis of polymer blends mixed with HIPS containing decabromo-diphenylethane (DDE) – the most common fire retardant for plastics used in the manufacture of TV and computer housings. Bhaskar et al. report that pyrolysis of these HIPS-based materials at 430 °C released 1,3-DPP and styrene in a 1:2 ratio, while pyrolysis at 330 °C released approximately twice as much 1,3-DPP as styrene! Thus we see that, in spite of RGJ’s claims to the contrary, there is abundant experimental evidence for the production of 1,3-DPP by the thermal decomposition of styrene-based plastics. In addition, the production of 1,3-DPP is expected to be particularly enhanced in the thermolysis of polymer blends and debris mixtures known to be present in the WTC rubble pile.

F. R. Greening  
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