Comment

Comment on Ernest et al. Programmable Thermal Dissociation of Reactive Gaseous Mercury, A Potential Approach to Chemical Speciation: Results from a Field Study. *Atmosphere* 2014, 5, 575–596

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The authors of this paper utilized a so-called "programmable thermal dissociation method" to monitor $HgCl_2$ emitted from a coal-fired Florida combustion plant. By comparison, they did confirm that the emitted mercury compound was in fact the dichloride, which is in fact the only such plausible molecule for mercury. However, the subtle implications in the paper that the $HgCl_2(g)$ molecule is not thermally stable and can readily dissociate in the gas phase at temperatures below 300 °C is not consistent with a very broad spectrum of chemical information and clearly can be misleading and incorrect if not more fully explained.

Unlike elemental mercury, its dichloride is known as a corrosive sublimate and it is soluble in water. Its heat of formation and heat of vaporization are well known, providing a gas-phase heat of formation that indicates an atomization energy $D_{0,Atomization}(HgCl_2)_g = 445 \pm 5$ kJ·mol^{-1} [1,2], supported also by theory [3]. The monohalide, $HgCl(g)$, is well characterized and known to be very weakly bound, with $D_0(HgCl) = 96 \pm 8$ kJ·mol^{-1} (experimentally) [4,5] and 94 kJ·mol^{-1} (theoretically) [3,6,7]. Coupling these values implies the ClHg–Cl bond in $HgCl_2(g)$ has a bond strength of about 350 kJ·mol^{-1}. This is a significant strength and clearly indicates the unequal strengths of the two bonds. Its stability is the reason, in chemical equilibrium calculations describing combustion, why it is predicted that elemental Hg should be negligible and $HgCl_2(g)$ dominant [8]. The fact that it is not is due to the kinetic and time constraints on the formation mechanisms converting Hg to $HgCl_2$. Nevertheless, the thermodynamic calculations illustrate its bond strength and that it should be thermally stable below 500 °C, above which it does begin to thermally dissociate or be hydrolyzed by any gaseous water present. $HgCl_2(s)$ is very volatile and its vapor pressure is well established [2,9,10]. This increases rapidly in the 150–250 °C range (3 × 10^{-3} atm., 150 °C; 0.1, 228 °C; 0.2, 246 °C), with a boiling point of about 300 °C. Thermogravimetric measurements for $HgCl_2$ clearly indicate this rapid sublimation [11], and an attached atomic absorption analyzer confirmed the molecular nature of the vaporization [12]. No evidence was indicated for the presence of free Hg atoms while the mass decreased. The confusion has arisen from mercury's ability under certain conditions to release atomic mercury in nature from its molecules not only from oceanic sources but also from vegetation and soils [13,14]. This also has been apparent when $HgCl_2$ is absorbed into mixtures such as quartz, pyrex or ceramic wool, or activated charcoal [15], or may happen from the gypsum produced from combustor flue gas desulfurizers [16]. Although studied for many years, the mechanism for this chemical reduction and release still remains unknown [17,18].

In relation to coal combustion, this laboratory has monitored the induced conversion of Hg(g) to $HgCl_2(g)$ on passing coal-fired flue gases through a non-catalytic honeycomb carbon-steel metal insert held at temperatures in the region of 250 °C. This has now been confirmed in two coal-fired

pilot plant tests in which the mercury speciation and total mercury were monitored entering and leaving the thermostated insert using Tekran monitors that measure atomic, molecular and total gaseous mercury [19]. This work has clearly indicated that $HgCl_2$(g) can be heterogeneously formed in transit through the insert with conversions up to >80%. Rather than dissociation, only formation of gaseous $HgCl_2$ was evident for a broad temperature range, so claims of its instability under combustion conditions at low temperatures are not correct. What is being observed in this presently published case possibly remains uncertain. As to the nature of collection on the uncoated tubular denuders and whether this is the same as coating them with a standard chemical remains uncertain. The fact that similar vaporization curves were noted for the test and calibration does appear to confirm the results. Used in a broader, more complex mix application, it might be more difficult to analyze.

Conflicts of Interest: The author declares no conflict of interest.

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