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CASE REPORT

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Characterization of the Products Formed by the Reaction of Trichlorocyanuric Acid with 2-Propanol

ABSTRACT: We report a recent investigation into the death of a cat that was initially thought to involve intentionally burning the animal via the use of an ignitable liquid. The exposure of the animal to flame was ruled out. Instead, forensic investigation revealed the intentional mixing together of a common outdoor swimming pool chlorinator, trichlorocyanuric acid (TCCA), and 2-propanol (aka, isopropyl alcohol or rubbing alcohol). The reaction of these two chemicals resulted in the formation of cyanuric acid residue, hydrochloric acid, and the evolution of a significant volume of chlorine gas. Further α-chlorination side reactions also occurred between 2-propanol and TCCA to produce a variety of chlorinated 2-propanone species that were detected on the submitted evidence. The identification of the products of both the main reaction and the side reactions allowed the authors to determine what chemicals were originally mixed together by the culprit.

KEYWORDS: forensic science, 1,3,5-trichloro-1,3,5-triazinane-2,4,6-trione, trichlorocyanuric acid, trichloroisocyanuric acid, symclosene, cyanuric acid, 2-propanol, isopropyl alcohol, chlorine gas, animal cruelty

In September 2007, police responded to a report of a dead cat in an alley near a vacant lot in a residential neighborhood. The cat had sustained a head injury consistent with blunt force trauma, and parts of it appeared to have been intentionally burned by fire. A plastic bag was found near the rear paws of the animal and there were obvious burn marks at the point where the bag contacted the body. Close to where the cat lay was a plastic soft drink bottle. The bottle contained a white viscous liquid that had a very sharp "solvent" odor. This was one of several recent acts of cruelty against cats in the area and the community was becoming increasingly concerned that this apparent escalation in cruelty, if committed by one individual, was indicative of someone who may exhibit other antisocial behavior, including violence toward people (1,2).

Materials and Methods

Evidence Submitted

The initial police investigation focused on the possible use of an ignitable liquid to burn the cat. Police collected a sample of what they described as a "white viscous liquid" in a small metal tin, and had sealed the edge of the tin with tape. Six months after the incident they submitted the tin to our forensic laboratory for identification of the liquid; however, upon receipt it was found that the liquid had evaporated leaving an off-white colored, granular solid. The police also submitted parts of the cat fur which appeared to have been burnt requesting that the fur be examined for the presence of an ignitable liquid. Three weeks later, at the request of our laboratory, we also received the soft drink bottle found near the cat. Fortunately, the cap for this bottle had been found nearby in the alley and the attending police officer had tightly capped the bottle prior to storage. By the time the bottle was submitted the "white viscous liquid" had turned into a dark brown solid and had the consistency of a thick paste.

Gas Chromatography–Mass Spectrometry

Volatiles from each item were extracted onto an activated charcoal strip (ACS) purchased from Albrayco Laboratories (Cromwell, CT) using a passive headspace extraction method based on ASTM E1412 (3). The items were extracted for 16 h at either 60°C (i.e., heated) or room temperature. After headspace extraction, the ACS was eluted with 600 μL of carbon disulfide (Fisher Scientific, Nepean, ON, Canada) and a 1 μL aliquot of the resulting eluant was injected onto a gas chromatograph–mass spectrometer. The gas chromatography–mass spectrometry (GC–MS) analysis was performed on a 30 m × 0.25 mm i.d. × 0.25 μm film HPMS-1 capillary column (Agilent Technologies, Palo Alto, CA) using an Agilent 6890 gas chromatograph connected to an Agilent 5973 mass selective detector. The GC–MS conditions used were as follows: split injection (1:20) at 250°C, temperature programmed from 40°C (3 min isothermal) to 250°C at 8°C/min (post-run at 300°C for 5 min), and hydrogen carrier gas held at a constant flow rate of 1.2 mL/min. The detector was operated in the full scan mode (30–300 amu) with a sampling rate of 9.4 scans/sec. Mass spectral searches of the Wiley 275 Mass Spectral Library (1998) were conducted using Agilent ChemStation® software.

Fourier-Transform Infrared Spectroscopy

Solid samples were pressed into a thin film using a mini diamond anvil cell (High Pressure Diamond Optics, Tucson, AZ). The cell was mounted in a 6× beam condenser (Harrick Scientific, Pleasantville, NY) in a Thermo Nicolet 6700 Fourier-transform infrared (FTIR) spectrometer (Waltham, MA). The spectrometer used a cesium iodide beam splitter and a deuterated triglyceride sulfate detector to collect spectra between 250 and 4000 cm^{-1} at 4 cm^{-1} resolution.

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Powder X-Ray Diffractometry

X-ray diffractograms were collected using a Bruker D8-Discover micro X-ray diffractometer (Madison, WI) fitted with a Cu X-ray tube (type K FL Cu 2 K) operating at 40 kV and 40 mA, a 0.50 mm collimator, and a general area detection diffraction system detector set at a distance of 30 cm. The sample was pressed flat on a polished, 50.8 mm diameter silicon wafer (Institute of Electronic Materials Technology, Warsaw, Poland) and mounted on the horizontal stage of the diffractometer. Six frames were collected (theta/theta angles 8/8, 16/16, 24/24, 32/32, 40/40, and 48/46) with a dwell time of 360 sec per frame. Individual frames were stitched together using DiffractPlus® (Bruker AXS) and the resulting diffractograms were searched against the International Center for Diffraction PDF-2 Database (Newtown Square, PA).

Reagents

Trichlorocyanuric acid (TCCA), also known as trichloroisocyanuric acid, trichloro-*s*-triazinetrione or by its IUPAC name of 1,3,5-trichloro-1,3,5-triazinane-2,4,6-trione, was purchased from a local general retailer and was manufactured under the brand name of Aquarius® by Sani-Marc Inc. (Victoriaville, QC, Canada), and 2-propanol (isopropyl alcohol) was purchased from Caledon Laboratory Chemicals (Georgetown, ON, Canada).

Results and Discussion

Based upon the investigating police officer's description of the contents of the bottle, and the reported burns to the animal, we initially examined the fur for the presence of an ignitable liquid using a passive heated headspace method commonly employed for this purpose (4). Although the tin of "viscous white liquid" had obviously evaporated during police storage, we also examined this material for ignitable liquid residues. No ignitable liquid was found in either sample, and the cat fur, not surprisingly, was found to contain a variety of aldehydes (5) and fatty acids.

We next turned our attention to identifying the off-white colored material in the tin. The FTIR spectrum, shown in Fig. 1, was tentatively identified as cyanuric acid by comparison with a spectrum from the NIST database (6). The white material was confirmed as cyanuric acid by X-ray diffraction analysis (Fig. 2).

By this time, we had received the soft drink bottle. The cap was removed and the bottle was placed into a new, 1 L metal paint can and the volatiles were extracted using a passive headspace method at room temperature. The contents of the bottle had a very sharp, acrid odor. Analysis of the volatiles by GC–MS showed that the bottle contained a variety of chlorinated compounds which were identified by their mass spectra as: 1-chloro-2-propanone; 1-chloro-2-propanol; 1,1-dichloro-2-propanone; 1,1,1-trichloro-2-propanone; and 1,3-dichloro-2-propanone (Fig. 3). Also present in the extract were two nonchlorinated compounds, 2-propanone and 2-propanol.

Cyanuric acid is most commonly used as a UV stabilizer for chlorine in outdoor swimming pools because it can bind hypochlorite ions thus slowing the loss of free chlorine due to exposure to sunlight (7). Cyanuric acid is introduced into swimming pools via its chlorinated analog di- or TCCA. A sample of "stabilized chlorinating tablets" (also known as swimming pool "pucks") was purchased from a local swimming pool chemical supply store, the label of which guaranteed it to contain 100% trichloro-*s*-triazinetrione (i.e., TCCA). In a fume hood, one TCCA acid tablet was crushed and 10 g of this granular powder was transferred to a disposable plastic beaker followed by the addition of 15 mL of 2-propanol. The TCCA and 2-propanol remained in contact, without visible reaction, for *c*. 30 sec, followed by a rapid reaction where the contents of the beaker bubbled vigorously and a greenish-yellow gas evolved. After the reaction the beaker was very hot to the touch. The disposable beaker and its contents were placed in a new, 4 L paint can, the can was sealed, and the volatiles were extracted using the passive headspace method at room temperature. The reaction of TCCA with 2-propanol produced the same chlorinated compounds found in the soft drink bottle together with 2-propanone and 2-propanol. A white solid remained in the beaker after the reaction and was confirmed to be cyanuric acid by FTIR and X-ray diffractometry (XRD) analysis.

As a final step, a small portion of the dark brown solid from the soft drink bottle was allowed to dry to a solid and was analyzed by

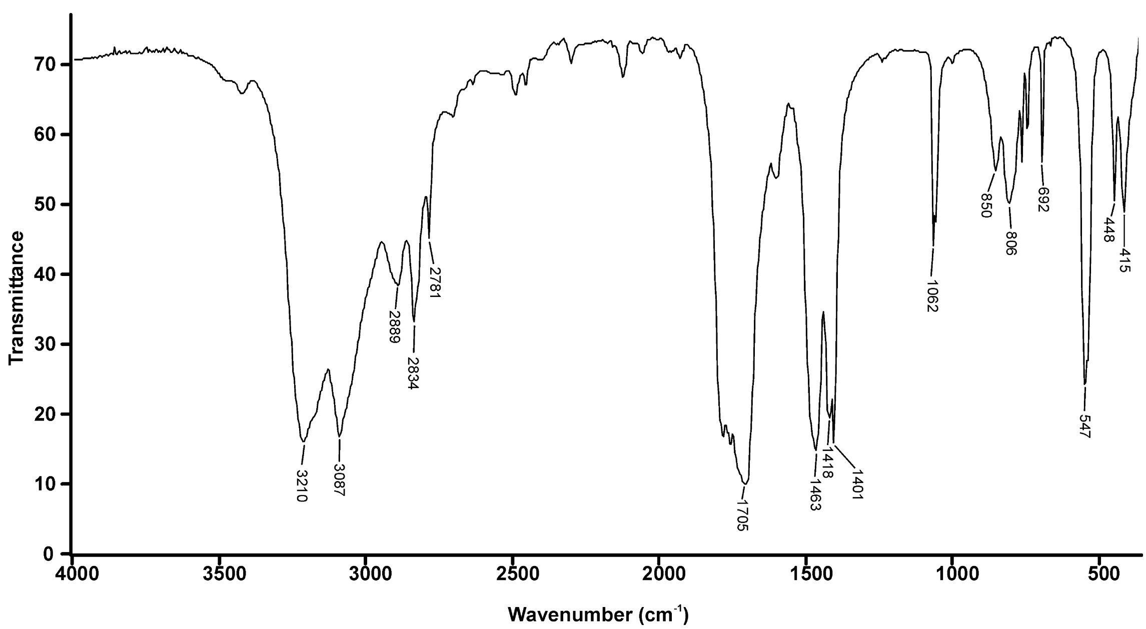

FIG. 1—*FTIR spectrum of cyanuric aid recovered from bottle.*

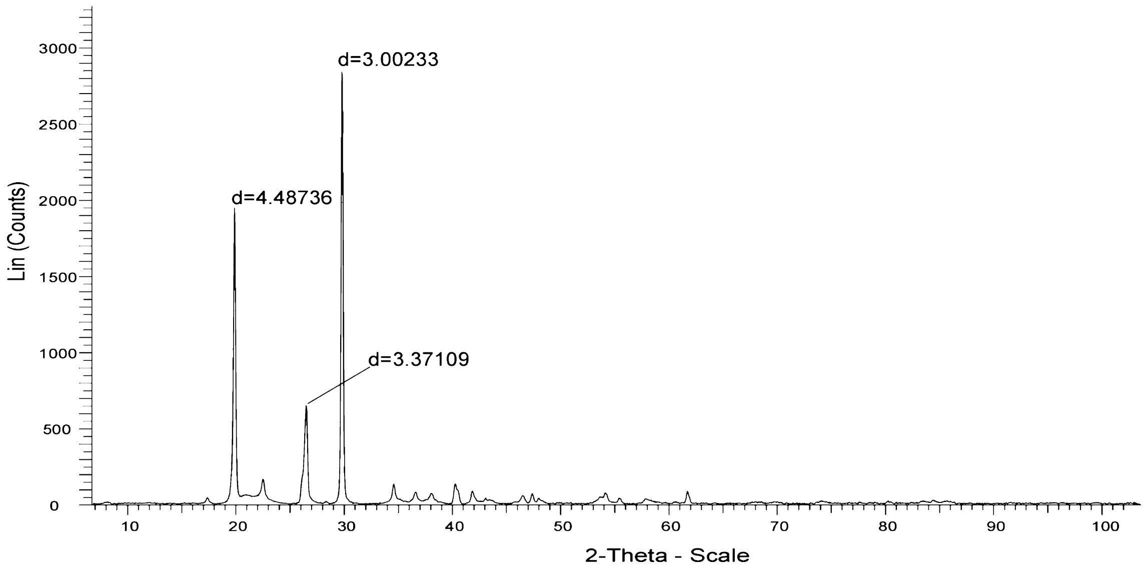

FIG. 2—*X-ray powder diffraction pattern of cyanuric acid recovered from bottle.*

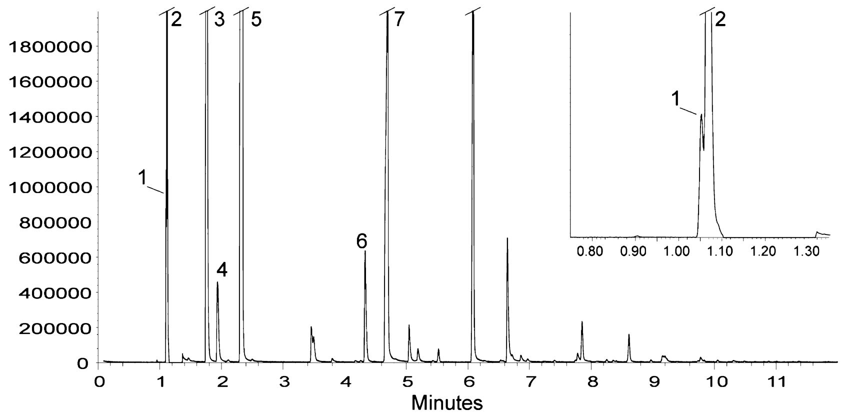

FIG. 3—*Chromatogram of volatiles recovered from bottle. Peak assignments are as follows: (1) 2-propanone; (2) 2-propanol; (3) 1-chloro-2-propanone; (4) 1-chloro-2-propanol; (5) 1,1-dichloro-2-propanone; (6) 1,1,1-trichloro-2-propanone; (7) 1,3-dichloro-2-propanone.*

XRD. The XRD analysis confirmed the presence of cyanuric acid. The source of the brown color was not pursued.

Cyanuric acid, together with melamine, has been recently reported as the cause of renal failure in dogs and cats and resulted in a major pet food recall (8,9). Protein testing methods for pet foods are based on nitrogen levels, and as cyanuric acid and melamine have high nitrogen content, they have been used as adulterants to artificially raise the apparent protein level of pet foods.

While cyanuric acid has been recently reported as a pet food adulterant, this was not the source of the cyanuric acid in this investigation. In this case, there was clearly an intentional mixing together of 2-propanol and either di- or TCCA to produce a chemical reaction. TCCA is often marketed under the name of its analog, trichloro-*s*-triazinetrione, for use as a chlorine stabilizer for outdoor swimming pools and spas. The explosive reaction of a mixture of two pool chlorinators, TCCA and calcium hypochlorite, in the presence of highly organic pool water has been reported (10); however, to our knowledge the results of mixing TCCA with 2-propanol by a member of the public has not been reported in the scientific literature. The reaction of di- and TCCA with simple alcohols was first reported by Walles and Nagy of the Dow Chemical Company (11). Walles and Nagy noted that this reaction would "generate sudden pressure" and that there was "a short delay between action and reaction." Experiments in our laboratory showed that granular TCCA mixed with 2-propanol would appear dormant for 20–30 sec prior to the rapid formation of gaseous products. The chief gas produced was chlorine gas as evidenced by the generation of a large quantity of green-yellow gas. Chlorine gas can form hydrochloric acid (HCl) and hypochlorous acid (HClO) in the presence of water, including moist tissue such as mucous membranes and the lungs (12), causing chemical burns (Fig. 4). In this case, natural moisture on the skin and fur of the cat may have reacted with the chlorine gas to give chemical burns that were mistaken by investigators for burns caused by heat.

To measure the amount of gas generated by this reaction, a simple eudiometer was constructed from a 100 mL graduated cylinder

$$Cl_{2(g)} + H_2O \rightleftharpoons HClO + HCl$$

FIG. 4—*Reaction of chlorine gas with water to produce hydrochloric acid.*

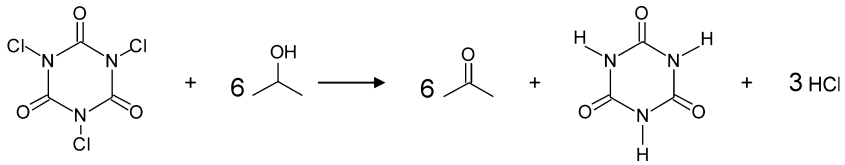

FIG. 5—*Oxidation of 2-propanol with TCCA to form 2-propanone (acetone) and hydrochloric acid.*

filled with water and inverted in a 2000 mL beaker filled with 600 mL of water. A piece of Tygon tubing was connected to the side arm of a 250 mL Erlenmeyer flask and run up into the inverted graduated cylinder. A 15 mL glass centrifuge tube was charged with 0.55 *g* of granular TCCA and placed into the Erlenmeyer flask. A graduated 10 mL pipette was used to deliver 4.0 mL of 2-propanol to the centrifuge tube and then the mouth of the flask was tightly closed with a rubber bung. No reaction took place for nearly 30 sec, after which time a significant volume of gas erupted from the mixture and rapidly filled the eudiometer. The mean volume of gas generated from three tests was 33 ± 7 mL (95% CI). The experiment was repeated, without closing the mouth of the flask, with a thermometer inserted into the reaction mixture. The maximum temperature recorded for the reaction was 69°C.

The use of TCCA to prepare ketones via the oxidation of secondary alcohols has been documented (13) and is key to understanding the products of the reaction of TCCA with 2-propanol. TCCA belongs to the family of *N*-chloroamines, a group of compounds that can function not only as chlorinating agents but also as oxidants by absorbing electrons (14). In this case, TCCA oxidizes 2-propanol to 2-propanone (acetone) and is itself reduced to cyanuric acid (Fig. 5). This oxidation–reduction reaction produces hydrochloric acid (HCl) as a byproduct; the hydrochloric acid thus generated promotes two subsequent reactions (Figs. 6 and 7). The remaining TCCA reacts with hydrochloric acid to generate chlorine gas and cyanuric acid by means of a second oxidation–reduction reaction (Fig. 6). The acidic conditions resulting from the initial reaction of 2-propanol with TCCA further promote an equilibrium between 2-propanone and its enol tautomer (Fig. 7). TCCA is also known to be a useful reagent for the chlorination of ketones in the α-position, a process which occurs via the enol (14,15). Alpha-chlorination results in the formation of the mono-, di-, and trichlorinated 2-propanone derivatives (i.e., 1-chloro-2-propanone, 1,1-dichloro-2-propanone, 1,1,1-trichloro-2-propanone, and 1,3-dichloro-2-propanone) detected in the reaction mixture (Fig. 7). The formation of a small amount of 1-chloro-2-propanol is interesting and originates, perhaps, via the reduction of 1-chloro-2-propanone. Note that in the laboratory the α-chlorination of ketones can be diminished and/or avoided if pyridine is added as a base to scavenge the released hydrochloric acid catalyst, thereby discouraging formation of the enol tautomer under acidic conditions (14).

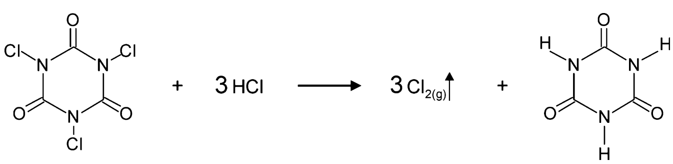

FIG. 6—*Reaction of TCCA under acidic conditions to produce chlorine gas.*

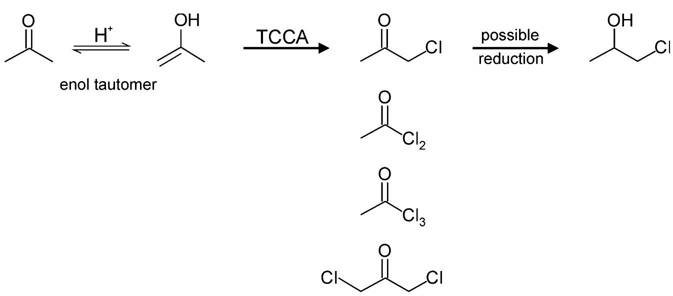

FIG. 7—*Oxidation–reduction reaction of TCCA and the enol tautomer of 2-propanone (acetone) to produce mono-, di-, and trichlorinated 2-propanone derivatives.*

A police investigation into a case of animal cruelty began with the police hypothesis that a cat, discovered dead from its injuries, had been set on fire with an ignitable liquid. However, subsequent forensic investigation ruled out the intentional setting of the animal on fire using an ignitable liquid. Instead, the forensic investigation revealed the presence of cyanuric acid, 2-propanol, 2-propanone, and various chlorinated derivatives of 2-propanone. The authors concluded that what likely took place was the intentional mixing of TCCA and 2-propanol in a plastic bottle, which resulted in the formation of copious quantities of chlorine gas. Exposure of the animal to the chlorine gas, in turn, likely caused the burns observed by police. It was not possible to determine if exposure of the animal to the chlorine gas contributed to its death, or if it was exposed to the chlorine gas after it had already been killed.

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