Review Article

"Breaking Bad" Television Series Explained to Students

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ABSTRACT

Objective: The classroom is an ideal environment to enhance the learning experience by the use of alternative media. In this paper we aimed to inspire a class discussion on the famous television series "Breaking bad", with the scope to analyze, interpreter and possibly explain all the chemical reactions and the bioactive toxic substances used during the episodes. **Methods**: We have found three main topics present in the series: i) methamphetamine preparation and its pharmacological effects, ii) explosives and inflammables, iii) poisons and other chemical substances mentioned in the series. **Results:** All these topics certainly are controversial but they are able to rise a prompt interest among the teenagers for topics such as organic chemistry, chirality, crystallography, purification of the substances, bioactivity, pharmacology and toxicology. However, the chemistry in the movie could be very misleading, overrated and imprecise, also the biological effects are artifact of the reality. **Conclusion:** We think that this paper could be used as guide to correctly understand TV series, prompting students to decide for themselves what is real or not. The drama characterized by the vivid images and sounds, as well as the occasional comic relief, promotes student engagement in the classroom more than a printed page.

Key words: Drugs, Pharmaceuticals, Hazards, Organic chemistry, Chirality, Multimedia-based learning.

INTRODUCTION

Learning process is a complex mixture of different factors which involves the school setting and outside forces as family, social community and informal experiences with television and technologies.[1] Television is a social media deeply eradicated in popular culture; it reflects the human's beliefs and behaviors. A huge amount of messages about science are present in movies and shows and may be successfully used by teachers as powerful teaching tools.[2]

Breaking Bad is an US television series created and produced by Vince Gilligan. The show originally aired on the AMC network for five seasons, from January 20, 2008, to September 29, 2013, rapidly became very popular among the teenagers due to the presence of explicit scenes of illegal preparation of methamphetamine and drug abuse. The plot is based on the history of a frustrated high school chemistry teacher Dr. White, that after being diagnosed with an inoperable lung cancer, becomes a clandestine "meth cooker" and later a criminal namely Heisenberg. Initially Dr. White justifies his criminal acts with the necessity to pay his medical bills and leave an economic future to his family before to die, in the end he will realize that he enjoyed to be a criminal being very good at it. However, even if this series was highly appreciated for its adherence to reality, in particular for the accurate description of the methamphetamine preparation, we feel that the numerous scientific experiments showed, the use of drugs, poisons, and several other chemicals need to be analyzed from a critical point of view, especially by the chemistry and pharmacy students, which should have the scientific bases to

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understand what appears in this television show. There are a lot of examples about the use of video clips to enhance the reinforce in the learning process.[3,4] Medical stories unit are also very popular to highlight the role of scientific process in diagnosis.

In this article, we took as example a TV series which still is very popular among the teenagers. The series have also a wide diffusion on the Web, being a social phenomenon. By analyzing the story, we took the chance to came across to several chemical processes and several misuses of bioactive substances, which are mainly unknown by the scholars e.g. ricin, covallatoxin, metamphamin, etc. Thus, it is important for the young students of Pharmacy, to understand the mechanisms of action of drugs, poisons, and some chemical reactions showed by the series.

The most important point is to sensitize the students of the Pharmacy Faculty to the dangers coming from the manipulation of hazards, and more of all to guide them to the understanding of the biological evidences of drugs abuse together with the social implications, in order to focus their attention on the scientific aspects of the topic more than on the trivial ones.

In this drama three main themes related to different chemistry areas have been presented and will be discussed in this paper:

Methamphetamine's preparation and its pharmacological effects;

Explosives and inflammables;

Poisons and other chemical reactions.

METHAMPHETAMINE'S PREPARATION AND ITS PHARMACOLOGICAL EFFECTS

Methamphetamine

Methamphetamine ("meth") is a stimulating drug of the CNS (central nervous system) initially used to fight fatigue of the night-shift workers and during the WWII by German to enhance the performances of the soldiers.[5] After the war it becomes available on the market as medicine to treat narcolepsy, depression, and severe obesity, lately ADHD (Attention-Deficit/Hyperactivity Disorder) in children and for the short-term treatment of obesity.[6] However, the prolonged use of meth can cause addiction and serious neurological damage. Due to its simple chemical structure, it is one of the favorite abused drug on the market; it is estimated that more than 1.3 million of people used meth in US.[7] Methamphetamine is the *N*-methylated analogue of amphetamine; thus they show the same mechanism of action promoting

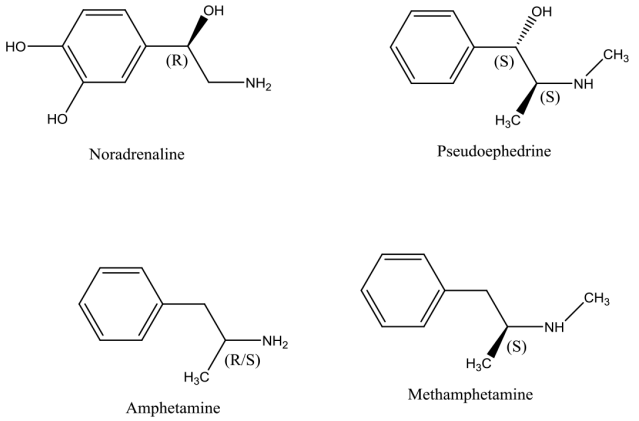


Figure 1: Chemical structures of methamphetamine, amphetamine, pseudoephedrine and non-adrenaline.

the monoamine's release from CNS with consequent stimulant behavioral effects (Figure 1).[8]

Methamphetamine also increases heart rate and blood pressure due to the release of norepinephrine from sympathetic nerve endings, thus can cause death at high doses.[8] Generally, amphetamine and its derivatives are used for both therapeutic and recreational purposes, but their administration's forms are different; the oral form of amphetamine to treat cardiac patients produces a slow-onset in 20-60 min, while aerial form of methamphetamine induces a fast-onset in a time range from seconds to min among crystal meth users: for example 20-25 mg of oral methamphetamine daily administered is required to cure the ADHD in children, while 40-60 mg of crystal meth is sufficient to have a significant rush.[9]

The quantity of crystal meth is strongly influenced by the pipe temperature, smoking technique, number of puffs and drug tolerance, which are related to the binge behavior of the users to reach higher drug doses.[10] Crystal meth (methamphetamine hydrochloride, "ice or Tina") is the smokable solid form of methamphetamine. It is a stimulant for recreational purposes preferred over the oral form for the rapid and intense "high" according to a potent drug addiction and other toxicities.[10]

In this administration form inconvenience and risks related to the intravenous form, are reduced but bioavailability is preserved. Chronic methamphetamine abuse induces psychosis with a collection of symptoms very close to those of schizophrenia, such as cortical GABAergic dysfunction,[11] finally provoking a collection of symptoms reflecting the Methamphetamine induced psychosis (MAP) model for schizophrenia.[11] Craving for crystal meth after stopping the abuse, is the principal withdrawal symptom caused by modifications in important neuronal functions.[12] And it can stand for years

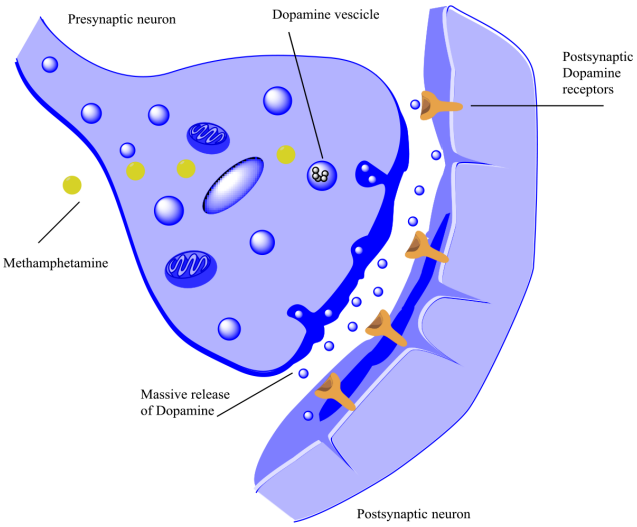
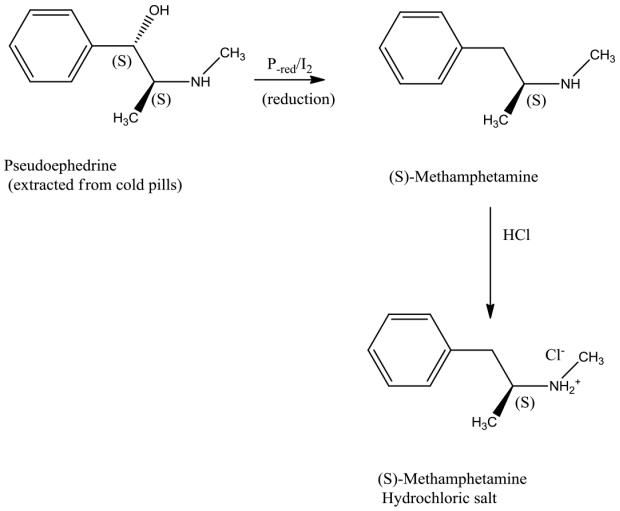


Figure 2: Mechanism of action of methamphetamine. Methamphetamine, doesn't act as a direct agonist of dopamine receptors. It is able to stimulate the secretion of catecholamines (in particular dopamine), which are normally stored in the deposit vesicles present in the pre-synaptic neurons. Methamphetamine and amphetamine also may acts as re-uptake inhibitor of catecholamines.



Scheme 1: Synthesis of Methamphetamine following the Nagai methods.

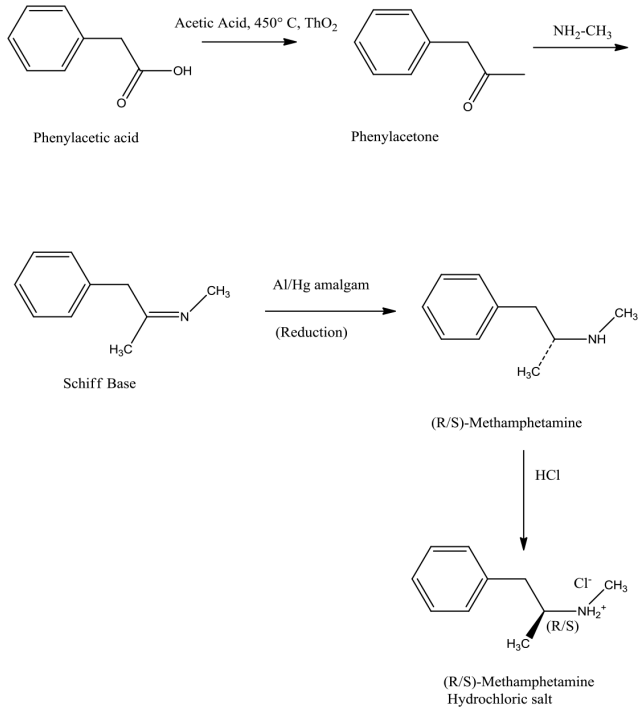
depending on physiology, the length of addiction/frequency and amount.[13]

It has been demonstrated that re-introducing the stimulant, the brain of the user can return to physiological conditions.[14] Strong dose of methamphetamine in animals harms striatal dopamine nerve terminals as well as for some methamphetamine users; Instead therapeutic doses of amphetamines don't damage the dopamine nerve terminal (Figure 2).[9]

Methamphetamine synthesis

The first synthesis of methamphetamine is showed in the first episode of Breaking bad; (S)-pseudoephedrine is extracted from legal nasal decongestant using various organic solvents and filtration through paper coffee filters. The pure isomer (S)-pseudoephedrine was transformed into (S)-methyl-amphetamine by reduction in presence of iodine and red phosphorus. In early episodes Walt and Jessie produced methamphetamine using the Nagai method, the first recorded methamphetamine synthesis,[15,16] which involves the reduction of pseudoephedrine with hydro iodic acid (HI) to give methamphetamine. Red phosphorus is necessary to reduce elemental iodine (I_2), extracted from disinfectants, to HI and to recycle reformed I_2; it is collected from matchbook striker pads or road flares which contain red phosphorous. The mixture is worked up by Dr. White in the pilot episode, by making the solution basic and then extracting it with an organic solvent. He used plastic syringe to remove the organic solvent layer, while chemists would use separatory funnels. Finally, the resulting D-methamphetamine is precipitated as HCl crystals, by bubbling the HCl gas into the solution (Scheme 1).

A possible alternative route is based on phenylacetone as starting material. The preparation of phenylacetone is made from phenylacetic acid, which is a legal substance (Scheme 2).[17] This is the second reaction used in the movie. In 1980 the DEA placed phenylacetone (P2P) into Schedule II of the Controlled Substances Act, making it illegal to buy, sell or possess without a controlled substance license.[18] Although P2P became harder to purchase, clandestine chemists synthesized P2P by themselves; in fact, Walt and Jessie claimed to prepare this precursor starting by Phenyl acetic acid and acetic acid (Scheme 2).[19] This reaction requires a catalyst, e.g. thorium oxide, made from thorium nitrate. This latest route is probably the one followed by Walter and Jesse. However, it should be noted that thorium nitrate is a quite rare catalyst, and its availability on the non-specialized market is unlikely. Then, once synthetized the achiral phenylacetone, the carbonyl group should react with methylamine to form immine intermediate (Schiff base) and the subsequent reduction will give the resulting racemic methamphetamine in a multistep or one-pot reaction. In Episode (s1 ep. 4) Walter and Jesse stated that Mercury aluminum amalgam can be a valuable catalyst, but the addition of aluminum foil into the reactor was only shown. Sodium amalgam or lithium aluminum hydride could be also employed as catalysts.[20] The reaction is not stereospecific thus the product is the racemate (S/R)-*N*-methyl methamphetamine, but unfortunately the technique used to solve the racemate resolution is not completely clear in the movie. In order to produce an enantiopure product, two ways are possible: (i) the



Scheme 2: Nagashi method for preparation of racemic methamphetamine.

use of stereoselective catalyst to give only one product optically pure; (ii) stereospecific separation involving the crystallization technique. Unfortunately, there is no indications about the method used in Breaking Bad. However, during several episodes, it is stated many time that the product was entantiomerically pure and the purity was close to 99%.

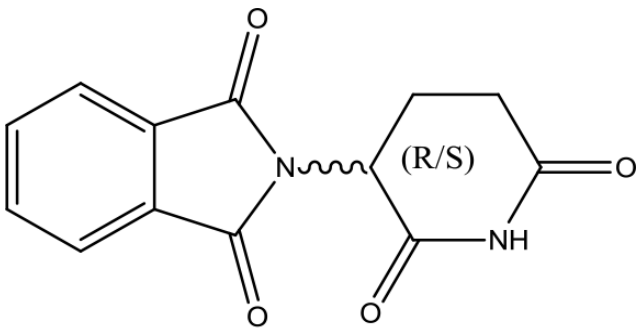
In the third and fourth series, it can be seen that the raw product come out the implant as oil that solidified in an amorphous glassy product by refrigeration with CO_2, and the actors break this glassy product by the hammer. Since Walt was claimed to be a brilliant crystallographer, we can suppose that crystallography is the easy and high yielding procedure performed to resolve the mixture, in which a chiral acid and the compound form a diastereomeric crystal.[21] Diastereomers possess diverse physical properties which facilitate the separation, but the procedure shown in the movie is not a chiral crystallization. From the 1960s to the mid-1980s clandestine methamphetamine producers performed reductive amination to cook meth ("crank" stands for methamphetamine in light of the Biker's transporting meth in the crankshafts of their bikes).[22,23]

In "Seven Thirty-Seven" (S.2E.2) Hank shows the video of the methylamine heist, and says: "P2P-they're cooking old school biker meth." This hints to the fact that reductive amination is less frequent today. In fact, DEA placed PAA on the "watch list" leading to the choice of the pseudoephedrine based syntheses.[18]

From 2005 Combat Methamphetamine Epidemic Act (CMEA) title VII restricts pseudoephedrine retail purchases and imposes to record all sales.[24] Pseudoephedrine reduction yields the D-methamphetamine while reductive amination gives the racemic D/L-methamphetamine mixture; [25] The first is much more potent than the racemic compound due to its chirality (not purity). Methamphetamine structure shows one chiral center thus it can exist as two mirror forms called enantiomers (R- and S-based on an assigned priority of substituent and D and L or (+) and (-) based on interaction with plane polarized light). Due to the chiral nature of pseudoephedrine and ephedrine, their reduction yields only D-methamphetamine. Dr. White clearly explains chirality concept by saying: "Just as your left hand and your right hand are mirror images of one another, identical and yet opposite, well so two organic compounds can exist as mirror image forms of one another". But then he wrongly recurred to the thalidomide case: its racemic mixture provoked major birth defects due to the effect of the less active enantiomer. But it has been demonstrated that the pure enantiomer of thalidomide converts in human organism due to the acidic hydrogen at the chiral center (Figure 3).[26]

Enantiomeric purity of methamphetamine crystals

Walt's methamphetamine was synthetized with the Nagashi method and it becomes blue after reductive amination. It is worth noting that the pure HCl salt of methamphetamine should be colorless-white crystalline solid, but illicit methamphetamine exists in a number of colors. The color could result from impurities formed during the reaction or for specific dye added to the crystals.[27] Profiling the impurities, an analytical chemist can often determine the method used to produce a sample



Thalidomide

Figure 3: Chemical structure of Thalidomide.

and even a minor amount (less than one percent) can influence a sample's color.[27]

The Walt's sample was claimed to be 99 percent pure and enantiomerically pure, however, the color and the lack of chiral selection would be not compatible with this statement. Several explanations have been done to the color of the methamphetamine produced in the series, the most probable accredited is that the color was just an invention of the producers, however, during the production of the show, DEA police officers helped the producers in order to ensure that certain critical steps of the actual meth preparations were omitted and that everything in this regard was kept legal.

EXPLOSIVES AND INFLAMMABLES

In the series, two explosives substance have been used by the characters in several situations. In this paragraph we explain their chemical composition, safety issues, and common uses.

The mercury fulminate is an explosive highly sensitive to friction and to mechanical shock, it is used especially in the production of detonators for explosives and primers for cartridges. It is prepared by mixing ethanol with a solution obtained by the action of concentrated nitric acid on mercury in presence of copper chloride as catalyst. Fulminated mercury was used by Dr. White to intimidate the drug dealer "Tuco" Salamanca. However, the crystals are quite different from that of methamphetamine and the reactivity of fulminated mercury was overestimated in the episode. Fulminated mercury [$Hg(CNO)_2$] is an explosive used as a trigger in blasting caps to set off larger explosives.[28]

Due to its instability, it can be detonated by friction, heat, spark, or shock.[28]

In the episode Dr. White requires a greater quantity of explosive with a much faster throwing velocity, such as that the final effect would be devastating for all.

Another substance used by Dr. White is "thermite". The thermite is the common name of a mix of metal powder, fuel and metal oxide (very close to black powder) that once ignited after heating, provokes an exothermic redox reaction.[29] It may be present in diverse compositions and different varieties are not explosive. Fuels incorporate aluminum principally, because of its high boiling point and low cost, magnesium, titanium, zinc, silicon, and boron. The Goldschmidt process is performed for thermite welding to join rail tracks, in metal refining and as pyrotechnic initiators in fireworks.[30]

Intense heat of thermite on a small area can cut through metal or weld metal components together both by melting metal from the components. Even if an industrial mixture thermite could be able to blow a door lock, the small amount used in the series is unlikely that would work in the way it was presented.

POISONS

Hydrofluoric acid

Hydrofluoric acid is usually sold in pressurized tank, but a colorless and highly corrosive solution of hydrogen fluoride (HF) in water is present in the movie. Hydrofluoric acid is able to dissolve glass and oxides that's why it is stored in plastic containers.[31]

Furthermore, it can penetrate tissue skin or eyes after inhalation or swallowing. Aqueous hydrofluoric acid is a corrosive liquid potentially deadly. Hydrogen fluoride is an extremely dangerous gas and an acute poison that may permanently damage lungs and the corneas of the eyes. LDPE (low-density polyethylene) the plastic polymer, has very low reactivity and it is not corroded by HF.[32]

In this case, the acid will primarily disintegrate the body, which as we know is about 80% water, thus creating a solution, but the non-reactive hydrocarbon of the bin would remain chemically inert. However, HF would not be able to liquefy the body to the substantial extent shown in the episode. Because it is a weak acid and exists primarily in its un-dissociated state, it is able to penetrate deeply into the skin before deprotonating, thus making it an excellent and efficient corrosive for human flesh; it reacts strongly with calcium and magnesium, so it would be able to efficiently dissolve bones.[31]

Other acids would be more helpful for the purpose such as sulfuric acid.

Phosphine

Phosphine (PH_3) is an inflammable and explosive gas with fish- or garlic-like odor,[33] highly dangerous on contact with air. By burning it produces a white dense fume of phosphorus pentoxide (P_2O_5) which is a respiratory tract irritant due to the transformation in orthophosphoric acid (H_3PO_4) reacting with water.

It causes peripheral vascular collapse, cardiac arrest and failure, and pulmonary edema.[33]

Systemic effects can derive from inhalation exposure, ingestion of metallic phosphides, and dermal contacts. It can be probably used as shown in the movie to intoxicate people or as poison.

Ricine

Ricine is a protein with cytotoxic bioactivity on eukaryotic ribosomes. It can be isolated from the plant of *Ricinus Communis* by hot extraction from the seeds.[34,35]

It has been nominated quite often in the series and it is finally used by Dr. White to kill Ms. Lidia in the last episode.

Different proteins of this family have been isolated from fungi (α-sarcin) and plants (ricin, abrin, and modeccin),[35] and they are able to inactivate 60 S ribosomial subunits irreversibly influencing the peptides elongation. Ricin and other plant lectins (e.g. abrin and modeccin), have two peptide chains A and B, joined together by a disulfide bond.[36]

The B-chain is responsible of the binding of the toxins on cellular surface receptors, while the A-chain promotes the enter in the cytoplasm to inactivate the 60 S ribosomal subunits. Despite the structural aspects, the mode of action of ricin and the other lectins is superimposed to that of α-sarcin for the following characteristics: (i) they influence EF-1' and EF-2 functions of 60 S subunits; (ii) energy and cofactors are not necessary. These evidences indicated that they also act on rRNA. In 1976 Mitchell *et al*.[37] discovered that ricin does not affect the sizes of rRNA species of L cell polysomes *in vitro*, let us supposing that the toxins are endonucleases; Obrig *et al*.[38] reported that the lectins, ricin and phytolaccin, and Shiga oxin hydrolyze naked 5S and 5.8S rRNAs. Recently, to test whether ribonuclease activity of ricin, if any, is involved in the inactivation of ribosomes, we determined the sequences of 5' and 3' termini of each rRNA species after ricin treatment and found that even 100 times molar excess of the toxin over ribosomes did not hydrolyze any rRNA species both exo- and endonucleolytically, consistent with the results of Mitchell *et al*.[37]

Ricin is considered a weapon of mass destruction, since its toxicity is so elevated that few milligrams are able to kill a man.

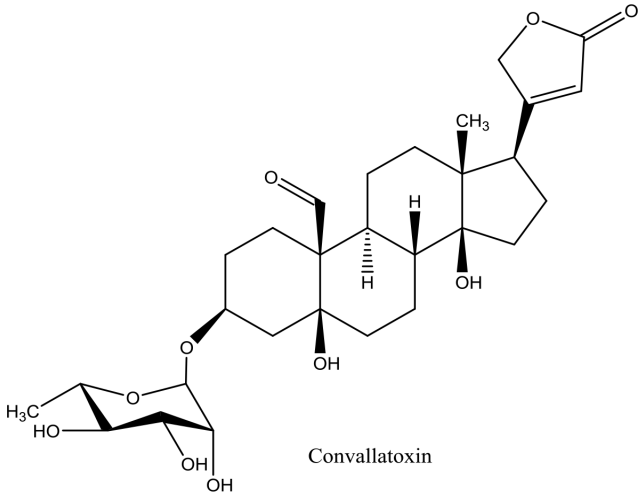


Figure 4: Structure of Convallatoxin.

Convallaria Majalis

Dr. White used this plant to poisoning the child of Pinkman girlfriend in order to turn him against Mr. Fring. The *Convallaria majalis* (also called Lily of the valley) berry intoxication is very common in the children, however, it is not lethal most of the time. It contains cardiac glycosides including convallatoxin (Figure 4) possessing cardiocinetic activities ten times greater than that of digitoxin: Therefore, not recommended for use without medical advice; it can have emetic action (stimulating vomiting), purgative drastic and cardiotoxic.[39]

It is worth noting that the plant used in the movie has no berries on it, thus the extraction of the poison would be impossible at that time.

Electrochemical reactions

Mercuric oxide Battery

The alkaline zinc/mercuric oxide battery is noted for its high capacity per unit volume, constant voltage output and good storage characteristics.[40] It is used in many applications where stable voltage, long storage time or high energy/volume rations are required such as in watches, pacemakers, and small electronic devices. During the last several years, the market for mercuric oxide batteries has almost completely evaporated, due mainly to environmental problems associated with mercury.[41]

In the TV series, Dr White built an electrochemical battery with several galvanized (plateled by zinc) metal objects, such as bolts, nuts, washers as anode, the breaks bad made of graphite and HgO, and sponges with KOH electrolyte solution as electrolyte to generate an ion conductor to link the two half cells reactors (*i.e.*, the anode (negative electrode) and the cathode (positive electrode)):

Therefore, the corresponding idealized electrode reaction should be:

$$Zn \rightarrow Zn^{2+} + 2e^- \quad (1)$$

$E_{0\ Zn/Zn2+}$ = -0.76 V under ideal conditions.

The reaction at the zinc negative electrode may be written:

$$Zn + 4OH^- \rightarrow Zn(OH)_4^{2-} + 2e^- \quad (2)$$

$$Zn(OH)_4^{2-} \rightarrow ZnO + 2OH^- + H_2O \quad (3)$$

These reactions imply the dissolution of the zinc electrode, with the crystallization of zinc oxide from the electrolyte. The reaction at the anode can be simplified to

$$Zn + 2OH^- \rightarrow ZnO + H_2O + 2e^- \quad (4)$$

At the Cathode: RV's brake pads (graphite blocks as electron conductor, coated with mercury oxide (HgO)). The electrochemical reaction may be written:

$$Hg^{2+}O + 2e^- + H_2O \rightarrow Hg + 2(OH)^- \quad (5)$$

The standard potential is

$E_{0\ Hg2+/Hg} = 0.85$ V

The total reaction of the galvanic cell should be:

$$Zn + Hg^{2+} \rightarrow Zn^{2+} + Hg \quad (6)$$

where the cell voltage can be calculated according to:

$$E_{cell} = E_{0\ Hg2+/Hg} - E_{0\ Zn/Zn2+} = 1.61\ V \quad (7)$$

However, the galvanic cells built in the episodes of the series don't work in ideal condition, and by using six of these cells the maximum voltage theoretically achievable was of 9.66 V. In a real condition, there is electrical resistance intrinsic to the circuits and on the conductor; also cars use a standard 12 Volt battery, with about 200-300 Amperes. The battery built by Dr. White surely wouldn't be able to start the RVD.[41]

CONCLUSION

Braking bad is one of the most popular television series of the recent years. It shows realistic and sophisticated organic reactions including clandestine methamphetamine preparation. However, the DEA itself participated to the script of the series to make sure that the detailed procedure will not be shown. Also several reagents, procedures and results are often imprecise, unexplained or voluntarily vague, in order to not be repeated at home. Also several points still remain obscure, *e.g.* how Dr. White prepared the domestic bomb that killed Mr. Fring, why his methamphetamine was blue, how he reached the chiral purity of the product by using an achiral reductive amination, how was possible to intoxicate the children if the *Convallaria majalis* L. did not have the berries, how was possible to make thermite from a little amount of aluminum oxide, finally the home-made battery will not be able to start the Van. The last consideration to be done on the surname chosen by Dr. White, Heisenberg. Heisenberg was a Nobel prize awarded German scientist that invented quantum mechanics and the "uncertainly principle".[42] However, as is Dr. White in the series, his genius was controversial, being a principal scientist in the Nazi German nuclear weapon project during World War II and at the same time claiming to have sabotaged the development of the nuclear bomb by the Germans. The role of television in enriching the popular culture is unquestionable, due to its potential to deeply affect viewers' thinking and imagination.[43]

The learning process is strongly fortified by this media because cognitive concepts are linked to emotional valence and pictures tell the story,[44] through episodic viewing programs that can be revisited in different times, in rearranged contexts for different purposes.[45]

Collective knowledge is increasing significantly today, but the multiplicity of Web content is always infested by misinformation and undetailed information on science,[46] but classroom discussions about scientific topic can be stimulated by teacher or students and the information coming from the media can be explained and criticized in a controlled environment.[47] This movie represents an exciting example of television sharing chemical knowledge.

ABBREVIATIONS

CNS: Central Nervous System; **Meth:** Methamphetamine; **ADHD:** Attention-Deficit/Hyperactivity Disorder; **MAP:** Methamphetamine; **US:** United States; **DEA:** Drug Enforcement Administration; **CMEA:** Combat Methamphetamine Epidemic Act; **LDPE:** Low-Density Polyethylene.

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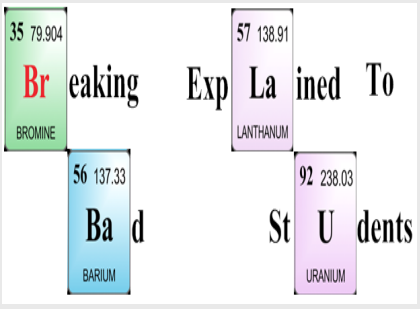
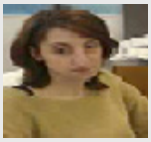
PICTORIAL ABSTRACT



SUMMARY

- Learning process is a complex mixture of factors involving schools setting, family, friends, community and social experiences with television and technology.
- Today young scholars are deeply attracted by TV series and telefilm, which represent a channel for learning and reach gradually experience on different concepts, for example chemistry topics.
- Breaking Bad is the most popular television series of the recent years, showing realistic and well detailed organic reactions, one of which clandestine preparation of methamphetamine.
- The story of Pinkman and Dr. White history is a pretext for sharing scientific knowledge with the public. Their personal life experiences are marked by moments of learning about the chemical discipline: electrochemical reactions, explosive and inflammables production, poisons.



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