

Synthesis of Organochlorine Herbicides and Comparative Evaluation of the Herbicidal Activities of their Acids and Alkali Metal Salts

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-----ABSTRACT -----

The drive to protect our environment from substances capable of disrupting the ecological equilibrium of the natural ecosystem necessitates detailed evaluation of non-target effects of substances such as herbicides used on our farmlands. In this study the herbicidal activities of sodium and potassium salts of Trichloroacetic acid (TCA) and 2,4-dichlorophenoxyacetic acid(2,4-D), representing the commonly used herbicides for monocotyledonous (grassy) and dicotyledonous (broadleaf) weeds respectively, have been evaluated. Trichloroacetic acid (TCA) was prepared by oxidizing chloral hydrate with concentrated tri-oxo-nitrate(V) acid while 2,4-dichlorophenoxyacetic acid (2,4-D) was prepared by treating 2,4-dichlorophenol with 50% 2-chloroacetic acid under thermostatically controlled reflux. The resulting herbicidal acids were converted to their sodium and potassium salts by treating each acid with a strong solution of sodium and potassium hydroxide. Comparative tests on plants revealed that the acid forms had stronger herbicidal properties than both sodium and potassium salts of the original products. Although the acids could attack older weeds much faster than the salts they had the potential of increasing the soil acidity to a level that may result in ecological mayhem. The tests further revealed that potassium salts of both TCA and 2,4-D were milder than the sodium salts of the two herbicidal acids; while the acid/salt blend in a proper ratio was found to reduce the soil acidity considerably. Thus the discernable difference in herbicidal strength of the acid and salt forms can be used as a guide to work out mixtures that are more environmentally friendly than the pure acids.

KEYWORDS: *Herbicidal acids, acids to salts conversion, soil acidity, environmental implication.*

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I INTRODUCTION

The quest for self-sufficiency in food production has generated a global concern over the years and the hope of achieving this feat has remained a mirage for decades, especially in the third world nations where agricultural mechanization is still wallowing in its infancy. Consequently nations all over the world especially the agrarian economies are still exploring the possibility of producing enough food to meet the demand of the ever-increasing population. One of the big steps taken in this direction is the use of herbicides as a cost-effective alternative to manual elimination of weeds, a development that has revolutionized the agricultural sector of many countries around the world. Obviously this has boosted food production to a large extent. However man's treatment of crops with foreign substances as a means of protecting them from their enemies and diseases [1] is not a measure devoid of environmental consequences. For instance works by the Environmental Protection Agency[2] identified herbicide contamination of surface waters as a major threat to aquatic ecosystems due its non-target effects. But considering the enormity of losses caused by weeds in our farms such as reduction in yield due to competition by the weed with crops for needed light and mineral nutrients [3], decrease in crop quality resulting from the shortage of their required needs for healthy growth, harboring of insects and other animals capable of destroying the crops etcetera, it is certain that weed is economically unfriendly and must not be left unchecked. In the light of the foregoing it is quite obvious that man must have begun the search for solutions to weed hazards even before the advent of modern agricultural techniques, although attempts to formulate an effective combatant were only in the realm of imagination. In practice four measures were adopted to limit the spread of weeds. These were manual weeding, crop rotation, ploughing and prevention of dispersal of weed seeds. The methods suffered basic limitations because they only aided to control but could not prevent weeds from growing with the crops.

What followed shortly after this period was introduction of weed-killing organic extracts and chemicals such as salts of inorganic elements and various industrial by-products. For instance, smelters' wastes were found to be effective in ridding the roadsides and paths of wild weeds [4].

Chemical weed-killing changed the paradigm of weed control in 1896 when Bonnet, a French grape grower, observed that the BORDEAUX MIXTURE (basic copper sulphate) he applied to his vine as a protection against downy mildew, turned the leaves of yellow charlock (*sinapis arvensis*) black [5]. The herbicidal properties of sulphate of some other metals were then soon observed. Following the sharp increase in demand for these chemicals with a subsequent rise in prices many people reverted to the use of ground-up pesticides such as nicotine, a compound extracted from tobacco; rotenone extracts from root of elliptica and pyrethrin extracts from pyrethrum flowers [6].

Although a few synthetic organic weed-killers such as 2-methyl-4,6-dinitrophenol or dinitro-o-cresol (DNOC) and a few more were known during this period, the most significant milestone in the history of chemical weed control roughly coincided with the onset World War II, when 2,4-D shown in figure 2(i) was discovered and used as the synthetic chemical defoliant for military purpose [7].

The discovery of 2,4-D was spectacular because it became known for the first time that a compound related structurally to a plant auxin (8) known as indol-3-acetic acid (IAA), first prepared by a German scientist named E. Fischer (1886), was capable of killing weeds selectively. The herbicidal activity 2,4-D ignited the present fast growing market [9] for broadleaf weed killers. Apart from 2,4-D other synthetic compounds related to IAA were applied to a wide range of plants and a number of physiological and morphological effects were observed by horticulturists and farmers. It was later found that many organic compounds when chlorinated at appropriate position possess some herbicidal properties. These compounds which take the general name Organochlorine herbicides form a large family in the entire class of organic and inorganic chemicals called pesticides. Although much has so far been achieved through the use of chemicals in fighting weed menace in our farms, it is worth noting that some of the commonly used herbicides especially those that are acid based [Table 3] are capable of causing ecological pollution. This work is therefore a deliberate attempt to convert typical herbicides with potentials to impact negatively on the ecological space to environmentally friendly substances through conversion of acid based forms to salts. The transformation of herbicidal acids to herbicidal salts may give birth to new generation of herbicides that will deal with the weeds with little or no adverse effect on the soil organisms and aquatic ecosystems.

II EXPERIMENTAL

2.0 Materials and Methods:

Chloral hydrate, Concentrated Tri-oxo-nitrate(v)acid, sodium hydroxide, potassium hydroxide, Potassium hydroxide pellets, 2,4-dichlorophenol, Methanol, distilled water, 2-chloroacetic acid, potassium tri-carbonate(iv), ethoxyethane, distilled water, concentrated hydrochloric acid and all other reagents were either purchased from standard Chemical Shops or sourced from the University of Calabar Chemical Store, and were of analytical grade.

2.1 Preparation of Trichloroacetic Acid

Trichloroacetic acid was first prepared by Dumas in 1838, by exhaustive chlorination of acetic acid in direct sunlight [10]. But now TCA is mostly prepared by oxidation of chloral hydrate with tri-oxo-nitrate(v) acid [11]. About 80g of chloral hydrate were placed in a 500ml three-necked Claisen flask. Heat was applied until the crystal just melted. Concentrated tri-oxo-nitrate (v) acid (34ml) was cautiously added through a glass funnel. The reaction that occurred resulted in evolution of brown fumes suspected to be nitrogen dioxide. As soon as the evolution of gas ceased the apparatus was arranged for distillation and the intensity of heat was gradually raised to speed up the reaction as the mixture turned reddish brown. The colour change was accompanied by liberation of toxic vapour. At about 190°C the tap was clogged as dense fumes evolved and the brown condensate (which later turned green) began to drop. At 194°C the collecting vessel was replaced with a conical flask (embedded in the ice-bath) to collect the condensate dropping at the temperature range of 194 – 196°C. The yield of the acid was 41.40g against the expected yield of 50g.

2.1.1 Preparation of Sodium and Potassium Salts of TCA

The sodium and potassium salts were prepared using sodium hydroxide solution. The solid TCA (12.80g) was placed in 125ml Erlenmeyer flask in an ice-bath and about nine-tenths (10.8ml) of an ice-cold solution of 3.20g sodium hydroxide pellets in 12ml of water was cautiously poured into the flask. A drop of 0.04% Bromocresol cream was added as indicator which turned the clear mixture faint yellow. With the aid of a

capillary dropping tube the remaining 1/10 (1.20ml) of the sodium hydroxide solution was titrated to a finish without any observable colour change. Additional amount of the hydroxide solution (0.6ml) on a further titration gave a colour change from faint yellow to greenish blue. Thus the volumes of the hydroxide solution summed up to 12.6ml. The mixture was gently evaporated for a few hours after which greenish white crystals of sodium trichloroacetate were formed. This method was also used in the preparation of potassium salts.

2.2 Preparation of 2,4-dichlorophenoxyacetic Acid

20g potassium hydroxide pellets were placed in a three necked-round bottom flask (500ml) followed by addition of 40ml distilled water. The mixture was swirled vigorously as the pellets dissolved to form a clear solution. 10g of 2,4-dichlorophenol was added to the solution followed by dropwise addition of 14ml of 50% 2-chloroacetic acid, and the system was then subjected to thermostatically controlled reflux. After 15 minutes of heating additional 14ml of the acid was added as the colour changed from light to deep orange. The warm mixture was then poured into a 500ml Erlenmeyer flask containing 100g cracked ice as the mixture turned grey. On acidification with conc. Hydrochloric acid (20ml) effervescence occurred and the mixture was cooled in the ice-bath to crystallize the acid. This was followed by extraction in ethoxyethane. The unused phenol was removed using 5% potassium tri-oxo-carbonate(iv). The aqueous solution of 2,4-D was acidified with concentrated Hydrochloric acid in an ice-bath and the precipitates formed were filtered using Buchner funnel. It was then recrystallized using 1:1 mixture of methanol and water. The yield obtained was 7.30g against the expected yield of 10g.

2.2.1 Preparation of Sodium and Potassium Salts of 2,4-D

6.40g of 2,4-dichlorophenoxyacetic acid was dissolved in 28.0ml sodium hydroxide solution prepared by dissolving 3.2g of the solute in 12ml of water. A drop of Bromocresol Green was added to the light blue pasty mixture and titrated with an additional amount (20ml) of sodium hydroxide solution without colour change. The mixture was then heated in the steam bath until the crystals of salts emerged. The sodium salt was filtered and preserved in a transparent bottle for application. The conversion of 2,4-D to potassium salt followed the same procedure except for a change from NaOH to KOH.

2.3 Methods of Application

In testing the herbicidal activities of the synthesized compounds one of the basic methods employed, was the post-emergence application. This involved application of herbicides on plants which have already grown out of the soil. The method was adopted to ensure that changes in the morphology of plants after application were easily monitored on a daily basis for a period of one week.

2.3.1 Field Application

The four varieties of herbicides prepared were applied on target representative weeds (Table 3) based on various concentrations (Table 2) and the herbicidal activity at a given concentration was monitored for a maximum of one week duration. All the concentrations for post-emergence tests were applied with a standard quantity (0.05%) of a non-ionic surfactant, prepared from a mixture of palmitic acid and ethanolamine.

Table 1: different concentration of 2,4-DNa, 2,4-D,Na-TCA,TCA

Weight of the salts (g)	Volume of water (cm ³)	Quantity in g/cm ³
0.5	100	5×10^{-3}
1.0	100	10^{-2}
1.5	100	1.5×10^{-2}
2.0	100	2×10^{-2}
2.5	100	2.5×10^{-2}

Table 2: The Representative Weeds Treated in Field Application

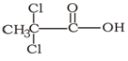
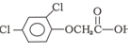
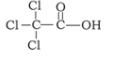

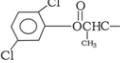
Broad Leafed Weeds	Grassy Weeds
Eupatorium odoratum	Axonopus compressus
Conyza aegyptica	Paspalum conjugatum
Ageratum conyzoides	Panicum maximum
Aspilia africana	Commelina benghalensis

III RESULTS AND DISCUSSION

3.1 Herbicidal Activities of TCA and 2,4-D

Trichloroacetic acid and 2,4-dichlorophenoxyacetic are among the commonly used organochlorine herbicides (Table 3) derived from acetic acid and phenoxyacetic acid respectively.

Table3:Some Acidic Organochlorine Herbicides in Common Use

S/ N	NAME	CHEMICAL STRUCTURE	USES
1.	2,2-dichloro-propionic acid (DALAPON)		Postemergent herbicides for grasses
2.	2,4-dichloro-phenoxyacetic acid (2-4-D)		Postemergent herbicide for broadleaf
3.	Trichloroacetic acid (TCA)		General post-emergent herbicide
4.	2,3,6-trichloro-benzoic acid (TBA)		Pre-emergent herbicide for broadleaves
5.	2-(2,5-dichloro-phenoxy) propionic acid		A broad spectrum hormone herbicide

However, TCA appeared to be much stronger than 2,4-D probably due to the presence of strong electron withdrawing species namely the three chlorine atoms directly attached to carbonyl carbon. This explains why TCA is the herbicide of choice for stubborn grass such *Axonopus compressus* (carpet grass). Thus TCA showed a higher herbicidal activity (Figs.4 and 5) than 2,4-D at equal and even at lower concentrations in spite of the fact that monocotyledonous species of weeds are naturally more stubborn than the dicotyledonous weeds. At the concentration 1.5% TCA showed herbicidal potency as its target grass became limp and wilted within 24 hours. While at the same concentration 2,4-D produced herbicidal effect after two days. Furthermore, it took 2,4-D about six days to kill weeds at the lowest concentration (0.5%) whereas TCA killed weeds at the same concentration within four days.

3.2 Herbicidal Activities of TCA-Na and 2,4-D-Na

The sodium salts of the two herbicidal acids showed relatively mild herbicidal effects on the representative target weeds. However, results of the test revealed that the sodium salt of TCA (TCA-Na) is a stronger weed killer than the sodium salt of 2,4-D. For instance at equal volume and concentration of 2.0% TCA-Na produced observable herbicidal effect on the target within one day, whereas at the same volume and concentration 2,4-D-Na only produced herbicidal effect barely two days after application [Figs1and2].

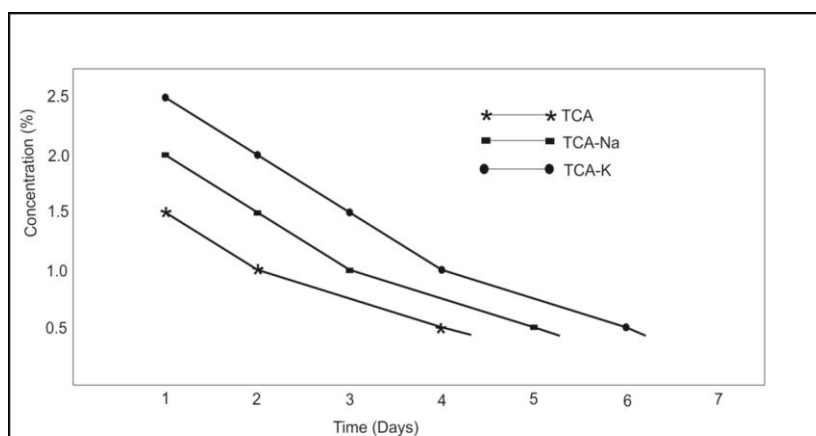


Fig 1: Herbicidal Activity Curves of TCA and its Na and K Salts

3.3 Herbicidal Activities of TCA-K and 2,4-D-K

The herbicidal properties of potassium salts of both TCA and 2,4-D are weaker than those of sodium salts discussed above. Nonetheless, TCA-K proved to be stronger than 2,4-D-K since the former showed marked herbicidal symptoms on weeds after a day and after six days of application with the maximum and minimum test concentrations of 2.5% and 0.5% respectively (Figs 1 and 2). On the other hand the potassium salt of 2,4-dichlorophenoxyacetic acid (2,4-D-K) produced effect at the two concentrations (2.5% and 0.5%) after two and seven days respectively.

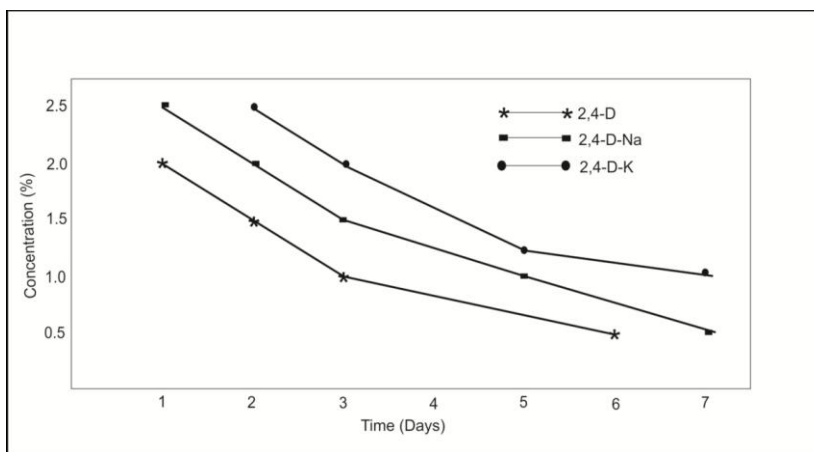


Fig 2: Herbicidal Activity Curves of 2,4-D and its Na and K Salts

3.4 Herbicidal Activities of Sodium and Potassium Salts of TCA and 2,4-D

The results of the tests as shown in the herbicidal activity curves (Fig.3) indicate that sodium salt of TCA is stronger than its potassium salt even though they are derivatives of the same acid. The fact is that the acidic property of sodium salt is higher than that of potassium salt because potassium is a stronger alkali metal than sodium and so sodium is bound to produce higher acidic effect just as laundry soap produced from sodium hydroxide is stronger than toilet soap produced from potassium hydroxide. It is worth noting that the herbicidal properties of sodium and potassium salts 2,4-D followed the same trends.

3.5 Herbicidal Properties of Herbicidal Acids/Salts Mixtures

Figure 3 shows variation in herbicidal activities of 1:1 mixture of the two acids and their metal salts. The results still put TCA and its sodium and potassium salt mixture ahead of 2,4-D and its mixtures, with TCA+TCA-Na showing the strongest herbicidal property, closely followed by TCA+TCA-K. However, at the concentrations of 2.5% and 2.0% TCA+TCA-K and 2,4-D+2,4-D-Na showed equal herbicidal activities as both of them wilted their targets within one and two days respectively. Beyond those concentrations TCA+TCA-K became more active than 2,4-D+2,4-D-Na until the minimum concentration of 0.5% when the herbicidal activity of the latter overtook that of the former. In any case 2,4-D+2,4-D-K showed the lowest herbicidal activity at every concentration applied.

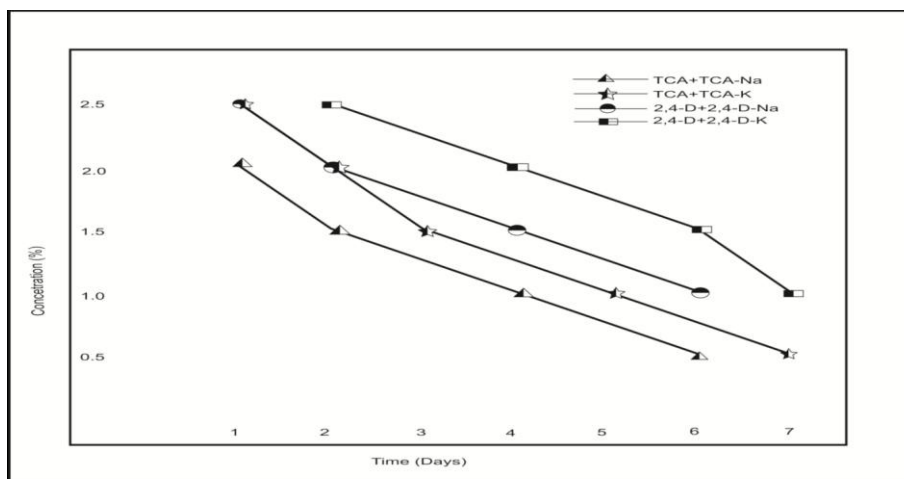


Fig. 3: Herbicidal Activities of 1:1 Mixture of TCA, 2,4-D and their Salts

3.6 Changes in Soil Acidity at Maximum Concentration after Test Duration

Soil acidity has a great deal of influence on the quality of plants since abnormally high acid in the soil can interfere with absorption of some plant nutrients as earlier noted. In this work the acidities of soil samples before and after herbicide application were determined by standard methods as soil P^H using Litmus Paper and confirmed electrometrically, using P^H Meter.

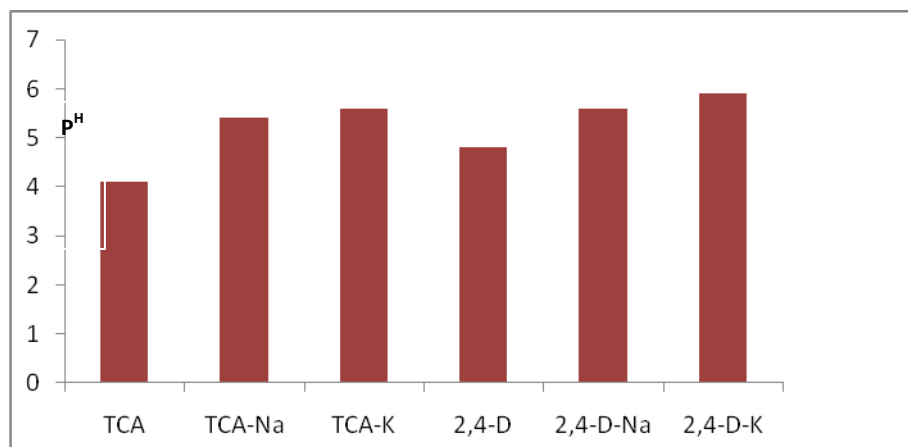


Fig.4: Changes in the Soil P^H at the Most Effective Concentration after 1Wk

Figure 4 above shows changes in soil acidity after one week of application of herbicidal acids and their various salts at the most active concentrations. The test depicts the soil treated with TCA as most acidic with a change in P^H from initial 5.05 to 4.30 corresponding to about 15% increase in acidity; while its sodium and potassium salts recorded changes in P^H values from 5.05 to 5.45 and 5.60 respectively, representing 8% and 11% drop in acidity. On the other hand 2,4-D soil sample showed 5% increase in acidity with a P^H change from 5.05 to 4.80, while the soil samples of its sodium and potassium salts gave a change in P^H values from 5.05 to 5.60 and 5.80 respectively, representing 11% and 15% decrease in acidity. It is obvious from the foregoing that the potassium salt of 2,4-dichlorophenoxyacetic acid is the least acidic of all the herbicides synthesized.

IV CONCLUSION

In our quest for improved yield of crops through application agrichemicals such as herbicides it is important to always evaluate the environmental implications associated with the products in order to strike a balance between crop yield and environmental safety both in long and short terms, since some of these chemicals have the potential to dislodge the equilibrium of our natural ecosystem. Thus, the study to comparatively evaluate the herbicidal activities of some of the commonly used organochlorine weed killers and their metal salts has been carried out. The study has revealed that herbicides applied in acid forms increased the soil acidity quite significantly and this may impact negatively on the population of the essential micro-organisms. Excess acid in the soil can also have detrimental effect on marine ecosystem when there is runoff of this toxic pollutants into our streams and rivers. On the contrary the herbicidal activity tests of their salt forms at all the test concentrations showed an appreciable reduction in soil acidity which of course qualifies them as more environmentally friendly agrichemicals. In the light of the foregoing it is worth recommending that herbicides be applied in their salt forms irrespective of how long it takes to produce the desired results, provided the safety of our environment is not compromised.

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