

**Research Article** 

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# Grindstone neutralization reactions for the preparation of various salts of carboxylic acids

### Abstract

According to green chemistry recommendations, avoiding usage of solvents during chemical reactions was considered as a modern approach in research worldwide. Usage of solvents usually associated with environmental impacts and chemical contamination besides the economical factor. So, it is highly recommended to undergo the chemical reaction without using solvents. Accordingly, our present study aimed to prepare carboxylate salts under solvent-free conditions. In this study, twelve salts like salicylate, oxalate, tartrate, and citrate have been prepared successfully in the form of sodium, potassium, and calcium salts using grindstone neutralization reactions between reactants in solid phase. Reactions under investigations were examined and evaluated in terms of initiating grinding time, practical percentage yield (%), and the released reaction temperature as-well-as the violence of the reaction. The reaction was affected greatly by acidity, basicity, and aromaticity of the reactants. It was found that sodium, potassium, and calcium salts of oxalate, tartrate, and citrate easily prepared within shorter time period (~1-4min.) with relatively high practical percentage yield (~ 60-85%). The violence of the reactions was monitored by recording the maximum elevated temperature which reached to 103°C after 2min. for the reaction of tartaric acid with NaOH. Aluminum salts of salicylate, oxalate, tartrate, and citrate were excluded from the grindstone neutralization reactions due to insufficient chemical reactivity of aluminum hydroxide towards carboxylic acids. It was found that salicylic acid is the lowest reactive compound due to its aromatic property, and therefore salicylate salts show the lowest percentage yield (~50-70%). Acidity and basicity are the main operational factors affecting on the chemical structure of the final product and its amount. The rate of changing temperature with grinding time ( $\Delta \phi$ , °C/min.) was calculated for the investigated reactions, and the reaction of citric acid with NaOH has the highest  $\Delta \phi$  value. Finally, the proposed chemical reaction is considered as good new water resources as-well-as simple preparation method for carboxylate salts. Grindstone neutralization reactions were characterized by simplicity, workability, applicability, efficiently in addition to shorter life time for the preparation of various salts of organic acids.

Keywords: grindstone, neutralization reactions, salicylate, oxalate, tartrate, citrate, organic acids, chemical resource of water

### Introduction

Salts of carboxylic acids are familiar and play an important role in so many fields, for example pharmaceutical,<sup>1</sup> food processing,<sup>2</sup> textile industry,<sup>3</sup> as-well-as preparation of the laboratory reagents.<sup>4</sup> From the chemical point of view, salts of carboxylic acids, RCOO<sup>-</sup>M<sup>+</sup>, are ionic organic compounds which are obtained by the reaction of carboxylic acid with reactive metals, metal oxides, hydroxides, carbonates, or bicarbonate. The majority of organic salts are soluble in water due to the presence of ionic bond, while alkyl groups (R) cause insolubility in aqueous solutions.<sup>5</sup> Carboxylate anion (-COO<sup>-</sup>) was described as hydrophilic or water-loving part in the salt, but alkyl and/or aryl groups (R, Ar) are the hydrophobic or water-repelling part in the molecule. Salts of carboxylic acids, like sodium salicylate, are an antiinflammatory agent<sup>6</sup> that is less effective than equal doses of aspirin in relieving pain and reducing fever. However, individuals who are hypersensitive to aspirin may tolerate sodium salicylate. According to American Medical Association (AMA) of Drug Evaluations, salicylate produces the same adverse reactions as aspirin, but there is less occult gastrointestinal bleeding.7,8 Sodium or potassium oxalate is used in finishing textiles and leather.9 It is a good reducing agent,10 and it can be used as a primary standard for standardizing potassium permanganate (KMnO<sub>4</sub>).<sup>11</sup> In the human body, calcium (Ca<sup>2+</sup>) and iron (Fe<sup>2+</sup>) react directly with oxalic acid to form oxalates crystals Volume 3 Issue 2 - 2019

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in urine. This forming carboxylic acid salt can accumulate as larger kidney stones that can stop the excretion of urine from kidney. An estimated 80% of kidney stones are formed from calcium oxalate.12 Magnesium (Mg<sup>2+</sup>) oxalate is 567times more soluble than calcium oxalate, so the latter is more likely to precipitate out when magnesium levels are low and calcium and oxalate levels are high. Rochelle salt or sodium potassium tartrate tetrahydrate (KNaC<sub>4</sub>H<sub>4</sub>O<sub>6</sub>•4H<sub>2</sub>O) is an odorless, colorless white crystalline solid with a salty taste. It is the double salt of tartaric acid. It is soluble in water but insoluble in alcohols. Commercially, Rochelle salt is prepared in aqueous medium by the direct reaction between potassium bitartrate and 0.5M Na<sub>2</sub>CO<sub>2</sub> solution. Rochelle salt as an additive having the symbol (E337) in food industry acts as emulsifier, stabilizer, buffer and antioxidant in cheese products, margarine, jellies, jams, minced meat, and sausage casings. Pharmacologically, it is used as saline cathartics (dose: 5 to 10g for adults), therefore it can be used for the removal of toxic materials in some cases of poisoning. Other applications include the preparation of piezoelectric crystals, in the manufacture of mirrors; in the plating industry; as a laboratory reagent; in the preparation of Fehling solution for the test of aldehydes13 and for delaying the quicksetting time of gypsum and cement.<sup>14,15</sup> Sodium citrate (E331) is the sodium salt of citric acid. Like citric acid, it has a sour taste. Like other salts, it also has a salty taste. It is commonly known as sour salt and is mainly used as a food additive, usually for flavor or as a

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preservative. According to the above mentioned applications and the usage of carboxylate salts, it was noticed that salts of organic acids play an important role in three main sectors

- a. Pharmaceutical and medical industry,
- b. Preservatives and food processing industry, and
- c. Laboratory chemicals or reagents.

Recently, the increase in demand for using salts of organic acids in various industrial sectors encourages many chemists and researchers to improve or enhance the preparation methods of these salts either at laboratory or industrial scale. Preparation of carboxylate salts usually associates with environmental issues and economic problems, especially with using solvents which easily spread the chemical contamination. Therefore, avoiding the usage of solvents during the preparation of carboxylate salts is the main target of environmental chemists, where the best solvent is no solvent.<sup>16</sup>Although, many organic compounds such as pyrazole chalcones,<sup>17</sup> α, β-unsaturated carbonyl compounds (Claisen-Schmidt condensation),<sup>18</sup> pyrimidine derivatives (Biginelli reaction),<sup>19</sup> and spiro indol derivatives<sup>20</sup> were synthesized by grindstone technique, but till now there is no trends in research to prepare carboxylate salts using the same technique. Literature show that the preparation of salts of carboxylic acid in aqueous medium is well-known, but its preparation without the usage of solvents is less known. So, our present work aimed to launch and evaluate the grindstone neutralization reaction technique for the preparation of salicylate, oxalate, tartrate, and citrate salts by the reaction with different alkalis in solid phase. Also, to study the chemical and physical changes that takes place during the chemical reaction. A comparison between different reactions was done in terms of the percentage yield (%), reaction time, and the released reaction temperature to show the structure behavior relationship for the investigated carboxylic acids.

### **Materials and methods**

### Chemicals, tools, and conditions

Salicylic acid (C7H6O3), oxalic acid (C2H2O4.2H2O), mesotartaric acid ( $C_4H_6O_6$ ), and citric acid ( $C_6H_8O_7$ ) were obtained from LANCASTER, ENGLAND. Table 1 shows the Chemical, structural, and physical characterization of various organic acids used in the present study. Pellets of potassium hydroxide KOH, pellets of sodium hydroxide NaOH, calcium hydroxide powder Ca(OH), and aluminum hydroxide powder Al(OH), were obtained from SURE CHEM PRODUCTS LTD, ENGLAND. All the above chemicals are analytical grade (≥99.90 %) and dehydrated for 24h in a desiccator contains dry lumps of caustic lime (calcium oxide, CaO) before using. Crystalline organic acids and alkalis were used in the solid phase without further treatment. A clean porcelain mortar with pestle was used for the neutralization reactions between organic acids and alkalis (grindstone preparation of organic salts). An electronic balance with four digits was used for weighing the solid reactants and products. The chemical reactions between organic acids and alkalis were carried out in the winter at the laboratory temperature ≈15±2°C, and humidity=83 % under a good ventilated atmosphere. Grindstone neutralization reactions are vigorous exothermic reactions leads to evolution of dense fumes/vapors and different odors, therefore the personal protective tools such as goggle, gloves, and the air filter, were used to protect eyes, hands, and the breathing system respectively during the experimental work. Also, the fuming cupboard was used for the very vigorous reactions to avoid the danger circumstances.

Table I Chemical, structural, and physical characterization of various organic acids

-	Organic acids						
Characters	Salicylic acid	Oxalic acid	Tartaric acid	Citric acid			
Structural formula (SF)	ОН	НО ОН		HO Citric acid			
Molecular formula (MF)	C7H6O3	C2H2O4.2H2O	C₄H <sub>6</sub> O <sub>6</sub>	C <sub>6</sub> H <sub>8</sub> O <sub>7</sub>			
Molecular weight (MW)	~ 138.12g.mol <sup>-1</sup>	~ 126.065g.mol <sup>-1</sup>	~ 150.00 g.mol <sup>-1</sup>	~ 192.12g.mol <sup>-1</sup>			
Classifications	Aromatic mono-carboxylic (mono-hydroxyl)	Aliphatic di-carboxylic (non-hydroxyl)	Aliphatic di-carboxylic (di-hydroxyl)	Aliphatic tri-carboxylic (mono hydroxyl)			
Number of carbon atoms	7C	2C	4C	6C			
Number of COOH group	I	2	2	3			
Number of OH group	I	0	2	I			
Melting point (MP), <u></u> C	158.6°C	101.5°C	165.5°C (meso)	156°C			
Physical state (at 25°C)	Crystalline solid	Crystalline solid	Crystalline solid	Crystalline solid			
Density (g.cm <sup>-3</sup> )	1.443	1.653	1.79	1.67			
pK <sub>a</sub> - values	pK <sub>a1</sub> = 2.97	pK <sub>a1</sub> = 1.27	pK <sub>al</sub> = 2.89	pK <sub>a1</sub> = 3.13			
	pK <sub>a2</sub> = 13.82	pK <sub>a2</sub> =4.27	pK <sub>a2</sub> =4.40	pK <sub>a2</sub> = 4.76			
				рК <sub>аз</sub> =6.40			

### **Grindstone neutralization reactions**

Different organic salts were prepared *via* the neutralization reactions between organic acids and different alkalis using gram molar

ratio. For the preparation of the carboxylate salts, 0.10Mole of the acid was reacted with the corresponding molar ratio of the alkali and the reaction proceeds according to the following general equations:

Dissociation of alkali:  $M(OH)_n \rightleftharpoons M^{n+} + nOH^-$  (1) Dissociation of an organic acid:  $nR-COOH \rightleftharpoons nR-COO^- + nH^+$  (2) Formation of carboxylate salts:  $R-COOH + MOH \rightleftharpoons R-COOM + H_2O$ .....(3)

Organic acid and alkali were mixed together by grinding the reactants for 1-4minutes using a mortar and pestle. During grinding process, the reaction was monitored by the thermometer, and after completion of the reaction, the product was subjected to drying into heating oven at 105°C to constant weight. The dry residue weighed and the percentage yield was calculated for each individual salt by the equation:

% Yield 
$$(practical) = \frac{(amount of residue (g))}{(total amount of reactants(g))} \times 100 = m / M \times 100.....(4)$$

After complete dryness, the chemical identity of the prepared compounds was confirmed practically by measuring the melting point of the dry salt using electric melting point instrument.

### **Results and discussions**

# Preparation of salicylates, oxalates, tartrates, and citrates

The reactions between organic acids and different alkalis to form various carboxylate salts has been carried out using grindstone technique, and the results of the reactions were summarized in Table 2, from which it was found that no reaction could proceed by direct contact between the reactants in solid phase without grinding, and this can be explained by the resulted friction between small molecules of the reactants from the mechanical grinding process is the initiating power of the neutralization reactions,<sup>21</sup> and the transferred energy

from the pestle to molecules is the driven force of the reaction.<sup>22</sup> It was noticed that aluminum hydroxide does not undergo grindstone neutralization reaction with any acids used in this study up to 10min. grinding time, and this is maybe attributed to the fact that aluminum hydroxide  $Al(OH)_3$  is considered as a Lewis acid (producing H+) of the lowest alkalinity that dissociates according to the following equations:

$Al(OH)_3 + H_2O \rightleftharpoons [Al(OH)_4]^- + H^+ \dots (5)$	
$\mathrm{H}^{+} + \mathrm{H}_{2}\mathrm{O} \rightleftharpoons (\mathrm{H}_{3}\mathrm{O})^{+} \dots \dots$	

The final product of the following overall reaction equation shows the actual structure of aluminum hydroxide is a coordinated complex having the formula  $[H_3O][Al(OH)_a]$  not  $Al(OH)_3$  as follows:

$$Al(OH)_{4} + 2H_{2}O \rightleftharpoons [H_{2}O][Al(OH)_{4}] \dots (8)$$

Table 2 Results	of grinding	reactions	between	various	organic	acids a	nd alkalis
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Reaction Mixture	%Yield	%Yield		Maximum	Violence	
Reaction Mixture	Theoretical	Theoretical Practical		Temperature (°C)	violence	
Salicylic acid + NaOH	89.83	70.2	4	33	Moderated	
Salicylic acid + KOH	90.68	70.73	4	30	Moderated	
Salicylic acid + $Ca(OH)_2$	89.7	50.64	6	17	weak	
Salicylic acid + Al(OH) <sub>3</sub>	89.03	0	10	Nil	No reaction	
Oxalic acid + NaOH	78.82	77.8	1.5	77	Vigorous	
Oxalic acid + KOH	82.09	80.89	1.5	70	Vigorous	
Oxalic acid + Ca(OH) <sub>2</sub>	78	60.65	3	30	Moderated	
Oxalic acid + Al(OH) <sub>3</sub>	74.65	0	10	Nil	No reaction	
Tartaric acid + NaOH	84.35	84	2	103	Vigorous	
Tartaric acid + KOH	86.18	85.22	2	100	Vigorous	
Tartaric acid + Ca(OH) <sub>2</sub>	83.89	61.97	4	40	Moderated	
Tartaric acid + AI(OH) <sub>3</sub>	82.18	0	10	Nil	No reaction	
Citric acid + NaOH	82.7	81.67	I	89	Vigorous	
Citric acid + KOH	84.93	84.05	2	85	Vigorous	
Citric acid + Ca(OH) <sub>2</sub>	82.14	66.32	3	35	Moderated	
Citric acid + Al(OH) <sub>3</sub>	80.01	0	10	Nil	No reaction	

Aluminum ion (Al<sup>3+</sup>) combines with three hydroxide anion (3OH-) and two water molecules via the formation of stable hydronium tetrahydroxyaluminate (III) complex as shown in equation (7 & 8).<sup>23</sup> Unfortunately, aluminum hydroxide exists as a stable coordinated complex instead of free available hydroxide anion form, and hence it was excluded for further or more investigations due to its low reactivity towards organic acids.24 Accordingly, it was concluded that aluminum salicylate, oxalate, tartrate, and citrate cannot be prepared using direct grindstone neutralization reactions. Besides, Table 2 refers to the presence of three types of grindstone neutralization reactions, vigorous, moderated, and weak reactions. Effervescence, evaporation, bubbles, and sudden increase in temperature were observed with vigorous reactions, but moderated reactions are less violent than vigorous reactions. Grindstone neutralization reaction of oxalic, tartaric, and citric acids with strong alkalis (NaOH & KOH) are vigorous reactions, while the reaction of salicylic acid with the same alkalis are moderated reactions. The last observation can be attributed to the fact that aromatic acids like salicylic acid are less reactive than aliphatic one.25 The lone pair of electrons of carboxylate anion (-COO<sup>-</sup>) in salicylic acid are delocalized and distributed on the benzene ring forming at least four canonical structures of carboxylate anion. Electronic resonance between carboxylate and benzene ring in salicylic acid supports the aromatic character of the molecule, and hence the stability of salicylic acid. The more aromatic character, the more stability of the molecule, and the low reactivity will be and the vice versa.5 The low reactivity of salicylic acid towards alkalis was confirmed by

- i. The relatively low percentage yield (practical) of the product,
- ii. The relatively more time for the reaction to begin,
- iii. Slight increase in temperature

Again, resonance and aromatic character of salicylic acid can explain the gap between the theoretical and practical values of the percentage yield for the reaction of the acid and alkalis. Mostly, reactions of investigated organic acids with calcium hydroxide can be described as moderated reactions and this are logically accepted due to decreasing in the basicity or alkalinity. The relative degree of violence of the reactions can be observed depending upon

- a. The recorded maximum temperature,
- b. The grinding time, and
- c. The percentage yield of the product

From Table 2 it was concluded that sodium, potassium, and calcium salicylate have been prepared successfully using grindstone neutralization reaction in shorter time (4-6min) with percentage yield up to more than 70%. Again, aluminum salicylate cannot be prepared using the proposed technique due to the low basicity of  $Al(OH)_3$ , and the low reactivity of salicylic acid. The expected reaction equations for the preparation of sodium, potassium, and calcium salicylate are:

 $C_7H_6O_3 + NaOH \rightarrow C_7H_5O_3Na + H_2O$  .....(9)

$$C_7 H_6 O_3 + KOH \rightarrow C_7 H_5 O_3 K + H_2 O \dots (10)$$

Theoretical and practical values for the reactions of oxalic, tartaric, and citric acids with strong alkalis are closely related to each other, while there are differences for the reactions with calcium hydroxide due to the low basicity of calcium hydroxide. According to the recorded maximum temperature and the practical percentage yield, grindstone neutralization reaction of organic acids with strong alkalis can be ordered as follows:

(Tartaric acid + MOH) > (Citric acid + MOH) > (oxalic acid + MOH) > (salicylic acid + MOH)

The above sequence may reflect the relative acidity and reactivity of the three acids towards grindstone neutralization reactions. Although the pK<sub>a</sub> values of the three acids prove that oxalic acid is the most acidic and citric acid is the lowest acidic one, grindstone neutralization reactions proves that acidity is not the only factor that playing role in the behavior of the acids during the reactions. Tartaric acid (di carboxylic acid) has the maximum percentage yield and recorded temperature and this may be due to the side reactions of the two hydroxyl groups (2OH) at C2 and C3 with alkalis forming sodium and/or potassium alkoxides (R-O-Na) compounds besides the main neutralization reactions of the carboxyl groups. Although citric acid contains three acidity sites, but it has not the highest released energy compared to tartaric acid, and this is may be attributed to the steric hindrance associated with the spatial configuration of citric acid. The higher steric hindrance, and hence the more crowding will be the lower availability of acidic center and vice versa. Sodium, potassium, and calcium oxalate can easily prepare in high percentage yield (>80.8 % with KOH) by the grinding technique in a short time (1.5-3min.) due to the aliphatic nature and the reactivity of the acid according to the following equations:

- $C_2H_2O_4 + 2NaOH \rightarrow C_2Na_2O_4 + 2_{H2}O + Energy \dots (12)$
- $C_2H_2O_4 + 2KOH \rightarrow C_2K_2O_4 + 2H_2O + Energy$  .....(13)
- $C_2H_2O_4 + Ca(OH)_2 \rightarrow (CO_2)_2Ca + 2H_2O + Energy \dots (14)$

Tartaric and oxalic acids have the same acidic nature, and are aliphatic di carboxylic acids<sup>26</sup> that can easily produce sodium, potassium, and calcium salts in the same manner with high percentage yield by means of grindstone technique. Tartrate salts can be prepared according to the following equations:

 $C_4H_6O_6 + 2NaOH \rightarrow C_4H_4O_6Na_2 + 2H_2O + Energy \dots (15)$ 

$$C_4H_6O_6 + 2KOH \rightarrow C_4H_4O_6K_2 + 2H_2O + Energy \dots (16)$$

$$C_4H_6O_6 + Ca(OH)_2 \rightarrow (C_4H_4O_6)Ca + 2H_2O + Energy \dots (17)$$

The results show that the reaction of tartaric acid with strong alkalis is vigorous and highly productive with short grinding time (2min). Citrate salts has been obtained by the grindstone neutralization reaction of citric acid with hydroxides of alkali and alkaline earth metal only. Citrate formation can be expressed as follows:

$$C_6H_8O_7 + 3NaOH \rightarrow C_6H_5O_7Na_3 + 3H_2O + Energy....(18)$$

$$C_6H_8O_7 + 2KOH \rightarrow C_6H_5O_7K_3 + 3H_2O + Energy.....(19)$$

$$2C_6H_8O_7 + 3Ca(OH)_2 \rightarrow (C_6H_5O_7)2Ca_3 + 3H_2O + Energy.....(20)$$

Water as a byproduct of the reaction and the physically adsorbed water molecules have been evaporated as a result of the released energy. The above neutralization reactions were initiated by grinding and an enhancement was introduced into the reaction through the first tiny amount of water produced during the reactions. This infinitesimal amount of produced water can complete the reaction by ion-exchange property between acids and bases. Identity of the prepared salts was confirmed by measuring the melting points, and the results show that the measured melting point of the prepared salts and the recorded values in literature are nearly the same.

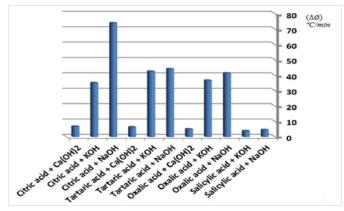
#### The rate of change of temperature with time

The variations of temperature during the grindstone neutralization reactions between organic acids and alkalis have been studied carefully, and the rate of change of temperature with grinding time  $(\Delta \phi)$  was defined as:

$$\Delta \varnothing = \frac{\Delta T}{\Delta t} = \frac{\left(T_f - T_i\right)}{\left(t_f - t_i\right)}, \mathcal{C}/\min \ or \mathcal{C}/s \qquad (21)$$

Where  $\Delta T$  are the temperature differences between the final temperature  $T_f$  and the initial temperature  $T_i=15^{\circ}$ C.  $\Delta t$  is the difference between final and initial time ( $t_f$  and  $t_i$ ). The values of ( $\Delta \emptyset$ ) were calculated for the active reactions between organic acids and alkalis, and the results were presented in Figure 1, from which it was noticed that all investigated reactions can be classified into three mean categories as follows:

- I. Reactions that have the highest rate of change of temperature with time (highest  $\Delta \emptyset$  value). The reaction of citric acid with sodium hydroxide represents this type of reaction ( $\Delta \emptyset$ =74°C/min.).
- II. Reactions that have the medium rate of change of temperature with time (medium  $\Delta \phi$  value). The  $\Delta \phi$  values of these types are in the range 35–44°C/min., and these reactions include the reaction of (1) oxalic acid with NaOH and KOH, (2) tartaric acid with NaOH and KOH, (3) citric acid with KOH only.
- III. Reactions that have the low rate of change of temperature with time (low  $\Delta \emptyset$  value), where  $\Delta \emptyset$  value is below 10°C/min., and these include the reactions of (1) salicylic acid with strong alkalis, and (2) oxalic acid, tartaric acid, and citric acid with Ca(OH),.



**Figure 1** The rate of change of temperature with time for different grindstone neutralization reactions.

The average rate of raising temperature is about  $\approx$ 4.125°C/min. or 0.069°C/s for the reaction with NaOH and KOH. According to the above mentioned results,  $\Delta \emptyset$  values for different alkalis and acids take the following sequences:

 $(\Delta \emptyset)$  for NaOH > $(\Delta \emptyset)$  for KOH >  $(\Delta \emptyset)$  for Ca(OH),

With the exception of (citric acid with NaOH):

 $(\Delta \emptyset)$  for Tartaric acid >  $(\Delta \emptyset)$  for Oxalic acid >  $(\Delta \emptyset)$  for Citric acid >  $(\Delta \emptyset)$  for Salicylic acid

The first sequence is in agreement with the alkaline properties of

these bases. For organic acids, the second sequence is in agreement with the results of citric acid which has a more crowded spatial configuration leading to shortage in the availability of acidic sites in the molecule. The reaction of citric acid with NaOH (exception) has the highest value of  $\Delta \emptyset$ , this is may be due to the small size of sodium ion (98pm)<sup>27</sup> which can easily overcome the steric hindrance and crowding in citric acid molecule. The smallest size of sodium ion can easily reach and facilitate the reaction with the three carboxylic groups in citric acid to form the sodium citrate salt with three acidic centers. From the above mentioned observations and according to the results in Figure 1 it highly recommended using the grinding technique for the preparation of sodium/potassium citrate, sodium/ potassium tartrate, and sodium/potassium oxalate in dry state. The process seems to be simple, having short time, having high percentage yield, and having high  $(\Delta \emptyset)$  value. Elevated temperature can help in producing a solid salt in dry state. Also, it highly recommended using the grinding technique for the preparation of calcium citrate, calcium tartrate, calcium oxalate, and sodium/potassium salicylate in wet state, where these reactions are having the lowest values of  $(\Delta \phi)$ . The elevated temperature in these cases is not enough to reach the complete dryness state.

# Grindstone neutralization reactions as a source of water

From the chemical equations of oxalic, tartaric, and citric acid with strong alkalis, water was produced as a byproduct of the reaction. So, grindstone neutralization reactions of carboxylic acids can be considered as new water chemical resources for places suffer from the scarcity of water like desert or moon. For astronauts, water is very big problem and the grindstone neutralization reactions of carboxylic acids maybe solving it by a simple chemical reaction. This reaction was completed within shorter time period (~1-2min.) to produce a reasonable amount of water, moreover the amount of heat evolved from the reaction with some of engineering modifications or designs may be leads to a new instrument that can condense and collect the water vapor in a receiving reservoir. The amount of water produced from the following mass balance equations:

Oxalic acid: (each 85g reactants  $\rightarrow$  18g of water)

$$C_2H_2O_4 + 2NaOH \rightarrow C_2Na_2O_4 + 2H_2O + Energy \dots (22)$$
  
(90g) (80g) (134g) (36g)

Tartaric acid: (each 115g reactants  $\rightarrow$  18g of water)

$$C_4H_6O_6 + 2NaOH \rightarrow C_4H_4O_6Na_2 + 2H_2O + Energy \dots (23)$$

(150g) (80g) (194g) (36g)

Citric acid: (each 104g reactants  $\rightarrow$  18g of water)

The above mass balance equations prove that oxalic acid is the mass favored compound that contain the minimum mass to produce the same amount of water. To produce one mole of water (18g), we need  $\frac{1}{2}$  moles (45g) of oxalic acid to react with one mole (40g) of NaOH. Besides the reaction temperature (77°C) is sufficient to evaporate the produced water molecules. We think that 36g (2moles) of water can save the astronauts' life for one day on the moon. It is great chemical reaction.

Grindstone neutralization reactions for the preparation of various salts of carboxylic acids

## **Conclusion and recommendations**

In this work, grindstone neutralization reactions between carboxylic acids (salicylic, oxalic, tartaric, and citric acids) and different alkalis were examined for the preparation of salicylate, oxalate, tartrate, and citrate salts. According to the present study, it is highly recommended to use NaOH and KOH for undergoing the neutralization reactions with aliphatic or aromatic acids. Salicylate, oxalate, tartrate, and citrate salts can easily prepared using grindstone neutralization technique with shortest time (1-4min.) and high percentage of yield (70-85%). The reaction of oxalic, tartaric, and citric acids with strong alkalis can be described as vigorous reactions having the highest rate of changing temperature with grindstone time. The investigated reactions produce water as a byproduct in a reasonable amount, so it would be considered a new chemical source of water for astronauts in the space. The research proposed and recommended to introduce some engineering modifications to the grindstone neutralization reactions to obtain the released water from the reaction. In general, the process seems to be very simple, do not need tools more than mortar and pestle, having good yield in shorter time, in addition to it is solvent free process.

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### **Conflicts of interest**

Authors declare that there is no conflict of interest.

### References

- Gupta D, Bhatia D, Dave V, et al. Salts of Therapeutic Agents: Chemical, Physicochemical, and Biological Considerations. *Molecules*. 2018;23(1719):2–15.
- 2. Nanditha M, Keerthi S, Birgitte KA. Biochemical Production and Separation of Carboxylic Acids for Biorefinery Applications. *Fermentation*. 2017;3(22):1–25.
- Sun D, Zhang X, Hui Du, et al. Application of liquid organic salt to cotton dyeing process with reactive dyes. Fibers and Polymers. 2017;18(10):1969–1974.
- Dorian AHH, Michelazzib M, Leonellib C, et al. The Effects of Carboxylic Acids on the Aqueous Dispersion and Electrophoretic Deposition of ZrO<sub>2</sub>. Journal of the European Ceramic Society. 2012;32(1):235–244.
- John D Roberts, Marjorie C Caserio. Basic Principles of Organic Chemistry. 2nd ed. Benjamin WA editor, Inc., ISBN 0-8053-8329-8.
- Preston SJ, Arnold MH, Beller EM, et al. Comparative analgesic and anti-inflammatory properties of sodium salicylate and acetylsalicylic acid (aspirin) in rheumatoid arthritis. *Br J Clin Pharmacol*. 1989;27(5):607– 611.
- https://www.ncbi.nlm.nih.gov/books/NBK218423/#\_\_NBK218423\_ dtls\_\_
- 8. https://pubchem.ncbi.nlm.nih.gov/compound/18943026#section=Top

- https://hazmap.nlm.nih.gov/category-details?id=17626&table=copytbla gents
- 10. https://www.ebi.ac.uk/chebi/searchId.do?chebiId=CHEBI:132764
- David Harvey. Modern Analytical Chemistry. New York: McGraw-Hill Companies; 2008. ISBN 0–07–237547–7.
- Coe FL, Evan A, Worcester E. Kidney stone disease. J Clin Invest. 2005;115(10):2598–2608.
- Hörner TG, Klüfers P. The Species of Fehling's Solution. European Journal of Inorganic Chemistry. 2016;(12):1798–1807.
- Maximilienne Bishop, Andrew R Barron. Cement Hydration Inhibition with Sucrose, Tartaric Acid, and Lignosulfonate: Analytical and Spectroscopic Study. *Industrial & Engineering Chemistry Research*. 2006;45(21):7042–7049.
- International Workshop on Calcium Sulfoaluminate Cements, Murten, Switzerland. 2018.
- Sheldon RA. Green solvents for sustainable organic synthesis: state of the art. Green Chem. 2005;7(5):267–278.
- 17. Pravina B Piste. Synthesis of Chalcones by grindstone chemistry as an intermediate in Organic Synthesis. *Int J Curr Sci.* 2014;13E:62–66.
- Hazarkhani H, Pradeep K, Sachin Kondiram K, et al. Highly Selective Claisen–Schmidt Condensation Catalyzed by Silica Chloride Under Solvent-Free Reaction Conditions. *Synthetic Communications*. 2010;40(19):2887–2896.
- Kumar JS, Shabeer TK. Multicomponent Biginelli Synthesis of 3,4-dihydropyrimidin-2(1H)-ones by grindstone technique and evaluation of their biological properties. *J Chem Pharm Res.* 2011;3(6):1089–1096.
- Sachdeva H, Sharma S. Green Preparation and Structure Elucidation of Spiro Indole Derivatives Using Grindstone Technique. *MOJ Biorg Org Chem.* 2017;1(5):170–174.
- Mogilaiah K, Kumara Swamy T, Chandra Vinay A, et al. Claisen– Schmidt condensation under solvent-free conditions. *Indian J of Chemistry*. 2010;49B:382–385.
- Fumio Toda. Solid State Organic Chemistry: Efficient Reactions, Remarkable Yields, and Stereoselectivity. Acc Chem Res. 1995;28(12):480–486.
- Geoff Rayner-Canham, Tina Overton. Descriptive Inorganic Chemistry. 5th ed. New York: WH Freeman and company; 2010. ISBN 13: 978-1-4292-2434-5.
- 24. Steven LN, Stanley LH. Kinetics of Acid Neutralization by Aluminum Hydroxide Gel. *Journal of Pharmaceutical Sciences*. 1976;65(8):1255–1258.
- Jonathan Clayden, Nick Greeves, Stuart Warren. Organic Chemistry.2nd ed. New York: Oxford University Press Inc., ISBN 978-0-19-927029-3.
- Solbes-García A, Miranda-Vidales JM, Nieto-Villena A, et al. Evaluation of the oxalic and tartaric acids as an alternative to citric acid in aqueous cleaning systems for the conservation of contemporary acrylic paintings. *Journal of Cultural Heritage*. 2017;25:127–134.
- 27. https://chem.libretexts.org/Courses/Mount\_Royal\_University/ Chem\_1201/Unit\_2.\_Periodic\_Properties\_of\_the\_Elements/2.08%3A\_ Sizes\_of\_Atoms\_and\_Ions