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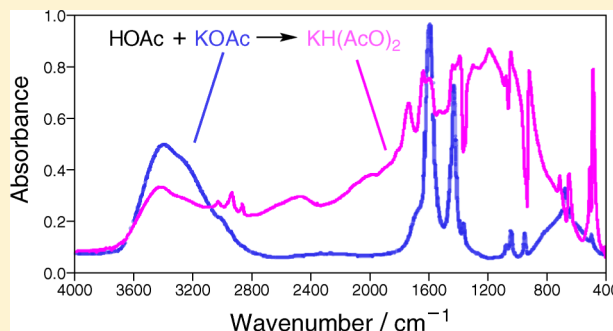
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ABSTRACT: The notion that acid salts exist only for diprotic and polyprotic acids is found in many high school and university textbooks, although the “only” condition is not always stated explicitly. A fairly simple experiment shows that there is a pronounced exothermic effect when pure acetic acid is added to potassium acetate. Experiments with similar reactions between other pure monoprotic acids and their corresponding salts were also carried out. In all cases, a pronounced exothermic effect could be detected and an explanation is offered in terms of formation of acid salts. All of the above salts contain strong hydrogen bonds in their structure (as may be unequivocally demonstrated by means of IR spectroscopy) and the existence of such intermolecular attractions is one of the factors leading to the exothermic effect.

KEYWORDS: First-Year Undergraduate/General, Upper-Division Undergraduate, Physical Chemistry, Textbooks/Reference Books, Acids/Bases, Bronsted-Lowry Acids/Bases, Carboxylic Acids, Hydrogen Bonding, IR Spectroscopy



The notion that acid salts¹ exist for diprotic or polyprotic acids can be easily seen in the majority of high school and university courses in general chemistry. It is fair to note that diprotic and polyprotic acids are not the *only* ones that can form acid salts. However, as stated by Goldberg:² “It is possible for an acid with more than one ionizable hydrogen atom (with more than one hydrogen written first in the formula) to react with fewer hydroxide ions, and to form a product with some ionizable hydrogen atoms left...”. The reader may be tempted to conclude that acid(ic) salts exist only for diprotic and polyprotic acids, but this would be incorrect as demonstrated in the next section. Even the excellent textbook by Whitten et al.³ makes no reference to the fact that acid salts may exist for many different acids. General chemistry textbooks, both old and new,^{2–6} seem to contain similar statements and do not mention any of the numerous examples of known acid salts. Perhaps textbooks do not mention such salts either because the salts are considered unimportant or because the authors are unaware that a monoprotic acid can form an acid salt. It is again fair to mention that in the *Dictionary of Chemistry*⁷ the reader meets examples for acid salts such as KHF_2 (potassium hydrogen fluoride) and $\text{Na}_3\text{H}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$ (sodium sesquicarbonate) showing that hydrogen salts can be formed by monoprotic acids (such as HF) and that diprotic acids could form *more than two* types of salts (Na_2CO_3 and NaHCO_3 in the case of H_2CO_3). The information found in this source seems to be enough for further examination of this topic.

The results of an informal poll performed on 47 university students from the first, second, and final year of study at our university showed that only one fourth-year student could give an example for an acid salt of a monoprotic acid (potassium

hydrogen fluoride was the only one mentioned). In fact, numerous examples of hydrogen salts of other monoprotic acids have been known in the chemistry literature for many decades. Thus, one could mention a series of acid salts of monocarboxylic acids, $\text{MH}(\text{RCOO})_2$, where M denotes an alkali metal and R stands for an alkyl group.^{8,9} It seems appropriate to mention that, in the anhydrous state, these acids exist in the form of hydrogen bonded dimers (Figure 1) and in some respect behave as diprotic acids. In aqueous solution, due to hydration, only monomeric $\text{RCOOH}(\text{aq})$ exists.

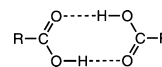


Figure 1. Hydrogen bonded dimers of monocarboxylic acids.

Other examples include acid salts of phosphinic acid, H_3PO_2 . This acid is monoprotic because two out of the three hydrogen atoms in the formula unit are bonded directly to phosphorus atom (Figure 2).¹⁰ The only possible potassium salt might be expected to be $\text{KOP}(\text{O})\text{H}_2$ but with an excess of the acid another product readily forms and (in agreement with its vibrational spectra) could be conveniently written as $\text{KH}[\text{OP}(\text{O})\text{H}_2]_2$.¹¹ An experimentally known example of an acid salt of nitric acid is $\text{CsH}(\text{NO}_3)_2$.¹² The crystal structure data¹² suggest that in the hydrogen dinitrate anion two of the $\text{N}=\text{O}$ bonds have bond orders (on the average) of 1.85, and that of the $\text{N}-\text{O}$ bond is 1.3. The bond order of each of the two $\text{O}\cdots\text{H}$ bonds is about 0.5. It is also worth pointing out the

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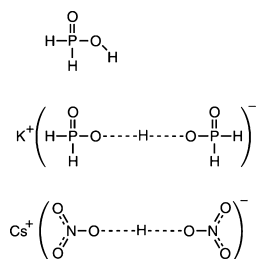


Figure 2. Structural formulas for phosphinic acid (top), $\text{KH}[\text{OP}(\text{O})\text{H}_2]_2$ (middle) and $\text{CsH}(\text{NO}_3)_2$ (bottom).

existence of several salts of the general formula $\text{M}_3\text{H}(\text{SO}_4)_2$,¹³ the latter example confirming that diprotic acids may form more than two types of salts. In the above cases, strong or very strong hydrogen bonds have been identified in the structure (Figure 2).

Considering the situation outlined above, a simple experiment is offered for convincing the reader that a chemical reaction between a “normal” salt of a monoprotic acid and the acid is possible, leading to an acid salt. The experiment was motivated by our earlier publication¹⁴ and might be useful for both high school and first-year university students. For graduate university students, a more involved proof based on IR spectroscopy is also offered.

EXPERIMENT

The formation of an acid salt can be demonstrated using simple equipment: a test tube filled with 1–2 g of a salt (potassium or sodium formate or acetate, etc.), a glass or a disposable plastic pipet filled with ≈ 1 –1.5 mL of the corresponding anhydrous acid (formic, acetic, etc.), and a thermocouple thermometer (the thermocouple probe is put in a thin glass tube, to protect the metals at the joint from the corrosive action of the acids). The temperature is monitored on the display of the digital thermometer. The experimental setup is presented in Figure 3. The IR spectra of the salt(s) (both before and after the reaction with the acid) are recorded on Perkin-Elmer System 2000 FT-IR spectrometer, from KBr pellets (about 1 mg of the sample is homogenized with 300 mg KBr and pressed). GRAMS 32 software (Galactic Industries Corporation) is used for all spectra manipulations.¹⁵

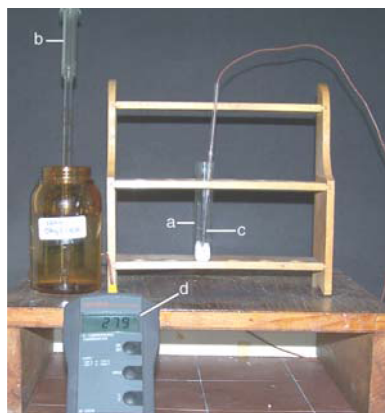


Figure 3. Experimental setup for the demonstration of chemical reaction between a salt of monoprotic acid, KA, and the acid HA: (a) test tube, (b) pipet, (c) the thermocouple, and (d) the screen of the digital thermometer.

HAZARDS

Anhydrous carboxylic acids (formic, acetic, etc.) are corrosive substances. Their vapors are highly irritating if inhaled. Always wear protective gloves and a face shield (or safety goggles) when performing the demonstration. Dispose the products (acid salts) under the drain with large quantities of water, or according to the local safety instructions.

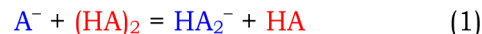
RESULTS AND DISCUSSION

Upon addition of the acid, a pronounced exothermic effect occurs with temperature increases ranging from 12 to 22 °C (Table 1). This may be taken as an indication of the formation

Table 1. Temperature Changes in the Reaction of Equal Quantities (≈ 0.01 mol) of Monoprotic Acid and Its Corresponding Salt

Acid	Salt	$\Delta T/^\circ\text{C}$
HCOOH	$\text{K}(\text{HCOO})$	18.9
CH_3COOH	$\text{K}(\text{CH}_3\text{COO})$	21.9
$\text{C}_2\text{H}_5\text{COOH}$	$\text{K}(\text{C}_2\text{H}_5\text{COO})$	12.5
HNO_3	CsNO_3	12.5

of the acid salt. Keeping in mind that the monocarboxylic acids in the anhydrous form, as mentioned above, exist as dimers, the neutralization reaction could be written as



Such carboxylate–carboxylate pairs (i.e., two RCOO^- anions bridged by a hydrogen atom) are known to exist and to be an important part of the so-called “catalytic toolkit” used in many enzyme reactions.¹⁶

An important property of the product is that it always contains very strong hydrogen bonds¹⁷ (Table 2 reviews the

Table 2. Crystallographic Measures of the H-Bond Lengths in Some Acid Salts of Monoprotic Acids

Compound	$R(\text{O} \cdots \text{O})/\text{pm}$
$\text{CsH}(\text{NO}_3)_2$	246.8 ^a
$\text{NaH}(\text{CH}_3\text{COO})_2$	244.4 ^b
$\text{KH}(\text{HCOO})_2$	244.7 ^c
$\text{KH}(\text{CH}_3\text{COO})_2$	247.6 ^c
$\text{KH}(\text{CF}_3\text{COO})_2$	243.7 ^c
$\text{KH}(\text{C}_6\text{H}_5\text{CH}_2\text{COO})_2$	244.3 ^c
$\text{KH}(\text{CH}_3\text{CH}=\text{CHCOO})_2$	248.8 ^c
$\text{KH}(\text{CHBr}_2\text{COO})_2$	244 ^d
$\text{RbH}(\text{CHBr}_2\text{COO})_2$	243 ^d

^aRef 12. ^bRef 9. ^cRef 18. ^dRef 19.

distances found in series of compounds by means of X-ray or neutron diffraction experiments). Normal $\text{O} \cdots \text{H} \cdots \text{O}$ hydrogen bonds feature $\text{O} \cdots \text{O}$ distances ≤ 300 pm. As seen in Table 2, $\text{O} \cdots \text{O}$ distances in carboxylate (and nitrate) acid salts are all ≤ 250 pm. Thus, all of these hydrogen bonds may be considered to be very strong. The pronounced exothermic effect is then expected as a direct consequence of the enthalpy of formation of the strong hydrogen bonds.

One might question whether the true cause for the pronounced exothermic effects may be associated with other types of changes in the system. To address these doubts, the infrared spectra were recorded of the normal salt (potassium acetate) and the product of the treatment of KCH_3COO with

CH_3COOH , that we claim to be potassium hydrogen acetate, $\text{KH}(\text{CH}_3\text{COO})_2$. The spectrum of the product, $\text{KH}(\text{CH}_3\text{COO})_2$, is strikingly different from that of the reactant salt, KCH_3COO (Figure 4). The continuous absorption

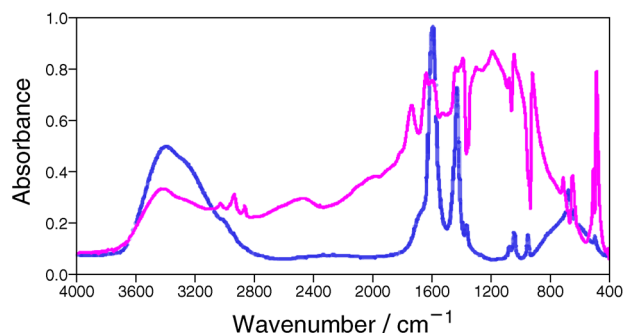


Figure 4. FT-IR spectra of KCH_3COO (dark blue) and $\text{KH}(\text{CH}_3\text{COO})_2$ (purple); the bands centered at $\approx 3400\text{ cm}^{-1}$ in both spectra are due to the stretching vibrations of adsorbed water. For purposes of presentation, the absorbance was normalized to 1.

centered at $\approx 1050\text{ cm}^{-1}$ in the FT-IR spectrum of the product (purple curve) is undoubtedly due to the O–H stretching vibration of the acidic proton and confirms the existence of very strong hydrogen bonds.²⁰ It is known that the O–H stretching vibration (the corresponding band can be very sharp in the absence of hydrogen bonding) shifts to lower wavenumbers and gains in intensity, as the hydrogen bond strength increases.²¹ One could also note that some of the bands (i.e., those at 1340, 1035, and 910 cm^{-1}) in the IR spectrum of KCH_3COO correspond to “Evans holes”,²² that is, transmission windows, due to peculiar type of quantum-mechanical resonance interaction between energy levels, on the broad O–H stretching band in the IR spectrum of $\text{KH}(\text{CH}_3\text{COO})_2$. However, these details are beyond the scope of the present article. As for the true chemical nature of the substance obtained in the reaction of KCH_3COO and HCH_3COO , it would be enough to say that our IR spectrum of the product claimed to be $\text{KH}(\text{CH}_3\text{COO})_2$ is practically identical to that reported in the literature.²³

CONCLUSIONS

The vast majority of students (and many teachers and instructors) think that monoprotic acids can form only normal salts, diprotic acids can form normal and hydrogen salts, triprotic acids can form normal and two types of hydrogen salts (monohydrogen- and dihydrogen-), and so on. This notion is wrong. Thus, sulfuric acid can form (in addition to the well-known sulfates and hydrogensulfates) at least two more kinds of acid salts: hydrogendisulfates, such as $\text{K}_3\text{H}(\text{SO}_4)_2$, and trihydrogendisulfates, like $\text{NaH}_3(\text{SO}_4)_2$. Other polyprotic acids behave analogously. Furthermore, as shown here, hydrogen salts exist for monoprotic acids other than HF. This contribution will hopefully fill the gap in the knowledge of both students and their chemistry teachers regarding the existence of various acid salts, particularly those of monoprotic acids.

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Notes

The authors declare no competing financial interest.

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