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Determination of the Number of Oxo Groups in Carbonyl Compounds Using the Potassium Iodate

Anitha Sudhir [1*], Sowmya P T [2]
[1*,2] Department of Chemistry, Vidyavardhaka College of Engineering, Karnataka, Mysuru

[*]**Correspondence**: Anitha Sudhir (dranithasudhir@gmail.com)

Abstract - Potassium iodate serves as a key component in a straightforward titrimetric method employed for quantifying the number of oxo groups in carbonyl molecules. This facile approach utilizes iodometry to gauge the remaining unreacted potassium iodate subsequent to the oxidative breakdown of the carbonyl molecule by potassium iodate. The examination of a diverse range of compounds for their oxo groups not only offers valuable information on molecular structure but also provides insights into the characteristics of these compounds. This knowledge holds significance across various disciplinary fields, enhancing our understanding of chemical reactivity and contributing to applications in the fields such as analytical chemistry, environmental studies, materials science, and pharmaceuticals.

Key Words: carbonyl compound, iodometry, oxo group, potassium iodate**.**

1.INTRODUCTION

Carbonyl groups, or oxy groups in short, are functional groups in carbonyl compounds that have two atoms of carbon double-bonded to one another. The polar nature of carbonyl compounds, their reactivity in nucleophilic addition and electrophilic substitution reactions, their capacity to form hydrogen bonds, their dipole-dipole interactions, resonance stabilization, and their adaptability to a wide range of organic molecules are the characteristics of oxygen groups. These characteristics are crucial to the chemistry of carbonyl compounds and the various chemical reactions and biological processes in which they are involved.

The diverse reactivity and functional qualities of oxy groups in carbonyl compounds, including amides, aldehydes, ketones, carboxylic acids, and esters, give them a broad range of applications in chemistry and industry. The essential building blocks of organic synthesis are carbonyl compounds. By means of processes like nucleophilic addition, condensation, and reduction, they are employed to produce increasingly complex compounds. They are necessary to produce fine chemicals, agrochemicals, and medicines. Carbonyl groups are present in a variety of flavour and aroma molecules. Plastics and synthetic polymers are made from monomers that contain carbonyl. They enhance the polymer's compatibility, adhesion, durability, and flexibility. They are utilized in paints, solvents, surface coatings, food preservatives, and flame retardants. They are therefore essential to contemporary chemistry and technology.

Potassium iodate (KIO_3) serves as an effective oxidizing agent in various chemical reactions due to its ability to readily donate oxygen atoms. As an ionic compound, potassium iodate contains iodine in its +5-oxidation state, making it a strong oxidizer. In reactions, it can transfer oxygen to other substances, promoting oxidation reactions by facilitating the loss of electrons. Potassium iodate finds applications in analytical chemistry, particularly in titrations where its standardized solutions are employed as oxidizing agents to determine the concentration of reducing agents. Additionally, its stability and predictable behavior make potassium iodate a valuable tool in laboratory settings for accurate and precise measurements.

Potassium iodate is often employed as a source of iodine. It undergoes a chemical reaction when treated with iodide ions in the presence of acid, resulting in the formation of iodine. The produced iodine is subsequently subjected to titration with a thiosulfate solution. Thiosulfate acts as a reducing agent and reacts with iodine. Scheme 1 illustrates the reaction pathway between potassium iodate and iodide ions. The liberated iodine reacts with thiosulfate in moderately acidic media (0.1 - 2.0 M HCl).

$$IO_3^- + 5\,I^- + 6\,H^+ \longrightarrow 3\,I_2 + 3\,H_2O$$

$$2\,S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2\,I^-$$

$$SO_3^{2-} + I_2 + H_2O \longrightarrow SO_4^{2-} + 2\,I^- + 2\,H^+$$

Scheme 1

Evaluating the number of oxo groups present in carbonyl compounds is crucial for a comprehensive understanding of their molecular structure, chemical characteristics, reactivity, and potential applications in various industries, such as environmental chemistry, materials science, medicines, fundamental research, and academic studies. This information plays a pivotal role in guiding experts and researchers in making informed decisions throughout the processes of synthesis, testing, storage, and application of these compounds.

In the domain of environmental chemistry, the identification and quantification of oxo groups contribute to assessing the impact of carbonyl compounds on ecosystems and human health. In materials science, understanding the presence of oxo groups aids in tailoring the properties of carbonyl-based materials for specific applications. In the field of medicine, knowledge about oxo groups is instrumental in designing pharmaceuticals with desired reactivity and therapeutic effects. Additionally, in fundamental and academic research, the comprehension of oxo groups in carbonyl compounds

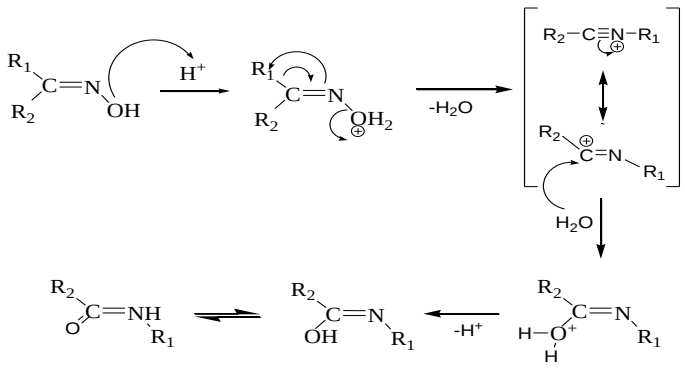
facilitates the exploration of new chemical reactions and the development of innovative methodologies.

By grasping the role of oxo groups, researchers can effectively navigate the complexities of carbonyl compounds, ensuring precision in their experimental approaches and advancing the potential uses of these compounds across diverse industries. This foundational knowledge underscores the importance of investigating the oxo groups in carbonyl compounds as a fundamental aspect of chemical research and application.

There are various approaches to determine the number of oxo groups, but the oxime method is the most popular one. Determination of number of oxo groups in carbonyl compounds through their oximes can be described by simple titrimetric method [1].

In our investigations, aldoximes have been observed to undergo quantitative oxidation to nitrile oxides, whereas ketoximes undergo direct and quantitative oxidation to iodonitroso compounds [2]. This method has proven valuable in various applications, such as studying iodine numbers in oils [3,4], determining the molecular mass of ascorbic acid in bulk and Vitamin-C tablets [5, 6], and exploring the Beckmann rearrangement.

The proposed reaction mechanism for the oxidative dehydrogenation of oximes (Scheme-2) involves the consumption of one molecule of potassium iodate per one molecule of the oxime. This reaction pathway provides insights into the transformation of oximes, elucidating the specific role of potassium iodate in the oxidation process. The versatility of the oxime method, coupled with its applicability in different contexts, underscores its popularity as a reliable and efficient approach for determining the number of oxo groups in carbonyl compounds. The findings from such investigations not only contribute to the understanding of chemical reactivity but also enhance the precision and reliability of analytical methodologies in various scientific fields.



Scheme-2

Experiment

Reagents

Oximes are chemical compounds derived from the reaction between a carbonyl compound (aldehyde or ketone) and hydroxylamine. They are commonly used in organic synthesis and can be characterized by the presence of the =N-OH functional group. The general method for preparing oximes involves reacting the corresponding carbonyl compound with hydroxylamine, often in the presence of an acid or base catalyst. The specific methods for each oxime may vary based on the starting material and reaction conditions.

Analytical reagent grade Ethyl methyl ketoxime, cyclopentanone oxime, cyclohexanone oxime, acetophenone oxime, benzaldehyde oxime, m-nitrobenzaldehyde oxime, p-methoxybenzaldehyde oxime, p-chlorobenzaldehyde oxime, 3,4-dimethoxybenzaldehyde oxime, 3,4,5-trimethoxybenzaldehyde oxime, and piperonal oxime were prepared by known methods [7] and 0.01 mol L^{-1} solution of potassium iodate using distilled water was prepared.

Results and Discussion

A precisely weighed (10–30 mg) oxime sample was dissolved in 5 ml of 95% ethanol in an Erlenmeyer flask and 20 ml of 0.01mol L^{-1} potassium iodate solution was added. The reaction mixture was kept at room temperature for varying time intervals (Table-1). By adding an equivalent volume of potassium iodate to the flask containing 5ml of 95% ethanol, a blank solution was prepared. A standard solution of sodium thiosulfate solution was used to titrate the iodine generated after adding 1mL of 1mol L^{-1}sulfuric acid, 1mL of 10% aqueous potassium iodide, and 2mL of water. Starch was used as an indicator at the end. The molecular mass of oximes was calculated empirically using the equation based on differences in the amounts of sodium thiosulfate solution consumed.

$$M_{oxime} = \frac{w \times 2000}{(V_1 - V_2) \times N} \qquad \text{... Equation 1}$$

Where V_1 and V_2 are the volume of the sodium thiosulfate solution consumed for the blank and actual experiment respectively. N is the molarity of the sodium thiosulfate solution used for the titration and w, mass of the oxime.

The molecular mass of each aldehyde and ketone containing one CO group is given by M_{oxime} - 15. Hence number of oxo groups (Table 2) present in the studied carbonyl compound is given by the following equation.

$$n = \frac{M}{M_{oxime} - 15} \qquad \text{...Equation 2}$$

where M is the studied carbonyl compound's molecular mass and n is the number of oxo groups.

Conclusion

Determining the number of oxo groups in a compound can provide valuable information about the compound's structure, reactivity, biological activity, environmental impact, and properties. This information is essential for chemists and researchers working in various fields, from synthetic chemistry to environmental science and pharmacology.

The average values of the molecular masses of several aldoximes and ketoximes were computed after 5 trials for each as shown in the Table1. All the samples' standard deviations were less than 1% of the molecular mass that was calculated. The number of oxo groups determined using equation 2 is shown in Table 2. Finding the number of oxo (carbonyl) groups in a compound is a crucial step in understanding its chemical structure and reactivity. It allows chemists to classify the compound and predict its behavior in various chemical reactions.

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Table 1. The Molecular masses of the oximes studied.

Oxime (Mol. Mass)	Reaction time (min)	Experimental values (Oxime taken in mg)					Average	Standard deviation %
		1	2	3	4	5		
Ethyl methyl ketoxime, (87.1)	30	87.56 (13.75)	86.97 (16.04)	87.28 (20.47)	86.43 (22.39)	87.12 (24,07)	87.07	0.42
Cyclopentanone oxime, (99.1)	2	99.34 (17.34)	98.61 (12.98)	98.58 (23.26)	99.38 (18.03)	99.41 (15.78)	99.06	0.43
Cyclohexanone oxime, (113.2)	2	112.84 (12.67)	112.63 (14.57)	113.29 (19.73)	113.52 (25.18)	113.36 (21.34)	113.13	0.38
Acetophenone oxime, (135.2)	15	135.56 (21.69)	134.89 (14.86)	134.73 (24.21)	134.62 (18.52)	135.29 (11.99)	135.02	0.40
Benzaldehyde oxime, (121.1)	6	120.58 (12.43)	120.71 (22.94)	121.49 (17.36)	121.29 (15.13)	121.37 (20.16)	121.09	0.41
m-Nitrobenzaldehyde oxime, (166.1)	4	165.62 (26.01)	166.45 (18.29)	166.39 (13.94)	165.79 (21.55)	165.91 (15.33)	166.03	0.37
p-Methoxy- benzaldehyde oxime, (151.2)	4	151.62 (11.99)	151.45 (25.81)	150.77 (21.29)	150.59 (16.47)	151.41 (13.66)	151.17	0.46
p-Chlorobenzaldehyde oxime, (155.5)	4	154.76 (17.39)	155.31 (19.22)	155.46 (23.14)	154.72 (12.15)	155.60 (15.92)	155.17	0.41
3,4-Dimethoxybenzaldehyde oxime, (181.2)	4	180.59 (22.63)	181.49 (25.12)	180.76 (12.98)	181.09 (16.25)	181.45 (19.01)	181.08	0.40
3,4,5-Trimethoxybenzaldehyde oxime, (211.2)	4	210.68 (20.85)	210.61 (12.71)	210.59 (15.03)	211.39 (18.72)	211.41 (13.84)	210.94	0.42
Piperonal oxime (165.1)	4	165.65 (18.04)	165.47 (26.01)	165.41 (15.81)	164.71 (12.42)	164.88 (23.93)	165.22	0.41

Table 2. The number of oxo groups present in carbonyl compounds studied.

Carbonyl compounds mol. mass (M)	Oximes (mol. mass)	Experimental average mol. mass of oximes (M_{oxime})	Number of Oxo group $n = \frac{M}{M_{oxime} - 15}$
Ethyl methyl ketone (72.1)	Ethyl methyl ketoxime (87.1)	87.07	1.0004
Cyclopentanone (84.1)	Cyclopentanone oxime (99.1)	99.06	1.0005
Cyclohexanone (98.2)	Cyclohexanone oxime (113.2)	113.13	1.0007
Acetophenone (120.2)	Acetophenone oxime (135.2)	135.02	1.0015
Benzaldehyde (106.1)	Benzaldehyde oxime (121.1)	121.09	1.0001
m-Nitro-benzaldehyde (151.1)	m-Nitro benzaldehyde oxime (166.1)	166.03	1.0005
p-Methoxy-benzaldehyde (136.2)	p- Methoxy benzaldehyde oxime (151.2)	151.17	1.0002
p-Chloro-benzaldehyde (140.5)	p-Chloro benzaldehyde oxime (155.5)	155.17	1.0024
3,4-Dimethoxy-benzaldehyde (166.2)	3,4-Dimethoxy benzaldehyde oxime (181.2)	181.08	1.0007
3,4,5-Trimethoxy-benzaldehyde (196.2)	3,4,5-Trimethoxy benzaldehyde oxime, (211.2)	210.94	1.0013
Piperonal (150.1)	Piperonal oxime (165.1)	165.22	0.9992