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Conductometric studies of mercury peroxychromate during its decomposition over conductivity water

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Abstract
The conductometric study of decomposition of mercury peroxychromate was done to determine the nature of mercury peroxychromate. At a particular temperature, the value of velocity constants are fairly constant which suggests that decomposition of mercury peroxychromate is of first order reaction.

Keywords: Mercury peroxychromate, conductivity water, conductometric study, order of reaction

1. Introduction

The chemical interest in understanding metal - dioxygen interactions, has led to the creation of the host substances containing transition metals that bind to and or react with dioxygen. While some of these substances may find use as materials or as industrial catalysts. They are also important to understand the active sites of biological dioxygen activators. The structure description of K_3CrO_8 provide a useful background and a good perspective of an extensive investigation of this group of compounds. Peroxo complexes of chromium, molybdenum, and tungsten are among the earliest known and best characterized. The vanadium peroxo compounds show to have biological as well as synthetic usefulness [1].In aqueous systems, the peroxychromate anion decomposes readily to release several species capable of causing lipid peroxidation. These species are hydrogen peroxide, hydroxyl ion, superoxide radical, singlet oxygen. Singlet oxygen produced by decomposition of peroxychromate has been suggested as one of the primary lipid oxidants. Decomposing peroxychromate has been used as a source of active oxygen species to examine their effects on biochemical functions [2-3]. Hydroxyl radicals are produced by decomposition of potassium peroxychromate that can peroxidize the unsaturated fatty acids of phospholipid dispersion [4]. Formation and decomposition of chromium peroxychromate was independent of hydrogen ion concentration and is of first order. Nature of peroxychromate was determined by various methods and metal peroxychromate was studied [5-12]. In the present work conductometric studies of mercury peroxychromate was done to assess the correct nature of mercury peroxychromate.

2. Experimental

The mercury peroxychromate was prepared by the action of ethyl acetate extracted hydrogen peroxide on solid dry mercury chromate. This was washed with ice cold water for several times to make it free from unreacted hydrogen peroxide. It is then kept in ice at 0 ^{0}C. For conductometric measurement “Doron” Conductivity Bridge was used. To start with the experiment the conductivity water was taken in a wide mouth pyrex tube, such that the platinum electrodes of conductivity cell were inside the aqueous layer, To it mercury peroxychromate was added and allowed to decompose in contact with water. The solution was thoroughly stirred for a moment before taking the reading and then allowed to separate in two distinct layers. The stop watch was started and simultaneously the conductivity was measured. The conductivity was measured at different intervals and process was repeated.
Since the conductivity of aqueous layer changed in a definite manner as decomposition of mercury peroxychromate proceeded, this physical property was made use in determining the rate of decomposition. It was found during the calculation that every stage had its own initial and final readings. Considering the process as a whole the calculation failed to show any particular order for the reaction. The reaction was considered as being made up of several stages. The final reading for the first stage of the decomposition was the measured of the

conductance at first break in the curve. This was also the initial reading for the second stage and the same was in case with all the stages. Every break in the curve corresponds to the end of the proceeding stage as well as the beginning of the succeeding stage. With these points in view the velocity constants, for different stages of the decomposition have been calculated as shown in the table from the expression: $K= \frac{2.303}{t} \log_{10} [\frac{a}{a-x}]$. Conductometric observations and velocity constants have been recorded in the tables.

Table 1

Time (Minutes)	Conductance X10-3	Time (Minutes)	Conductance X10-3
5	0.096	60	0.121
10	0.101	65	0.122
15	0.103	70	0.124
20	0.106	75	0.126
25	0.108	* 80	0.126
*30	0.108	85	0.127
35	0.111	90	0.128
40	0.114	95	0.129
45	0.116	100	0.129
*50	0.117	105	0.129
55	0.119		

* Breaks are obtained in the plot at the time values marked with asterisks

Mercury Chromate = 50ml... (A), Medium = Ethyl Acetate

Conductivity Water = 50ml.…(B), Ratio A:B = 1:1, Temperature =20° C

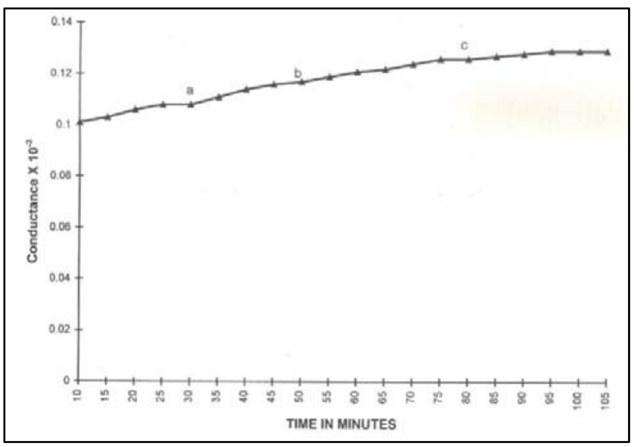

Fig 1: Decomposition of Mercury Peroxychromate prepared in Ethyl Acetate

Table 1.1: Velocity Constants of different stages of decomposition calculated from the observation of table 1.1A

First Stage			Second Stage		
Time (Minute)	a-x (a=0.108)	K	Time (Minute)	a-x (a=0.117)	K
10	0.007	0.27367	30	0.009	0.085513
15	0.005	0.20488	35	0.006	0.08488
20	0.002	0.19948	40	0.003	0.09160
			45	0.001	0.10584
Third Stage			**Fourth Stage**		
Time (Minute)	a-x (a=0.126)	K	Time (Minute)	a-x (a=0.129)	K
50	0.009	0.05279	80	0.003	0.047023
55	0.007	0.05256	85	0.002	0.049028
60	0.005	0.05379	90	0.001	0.054400
65	0.004	0.053086			
70	0.002	0.059198			

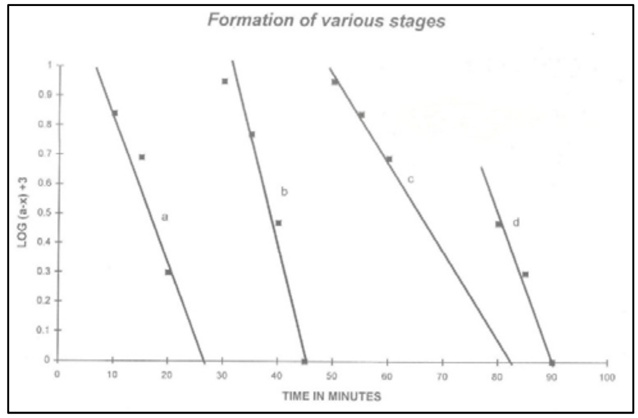

Fig1A: Formation of various stages

Table 2

Time (Minutes)	Conductance X10-3	Time (Minutes)	Conductance X10-3
5	0.095	60	0.114
10	0.097	65	0.116
15	0.099	70	0.118
20	0.101	75	0.120
25	0.103	80	0.122
*30	0.102	*85	0.122
35	0.104	90	0.125
40	0.106	95	0.127
45	0.108	100	0.130
*50	0.110	105	0.130
55	0.111	110	0.130

* Breaks are obtained in the plot at the time values marked with asterisks

Mercury Chromate = 30ml……. (A). Medium = Ethyl Acetate

Conductivity Water = 40ml…… (B), Ratio A:B = 3:4 Temperature =20° C

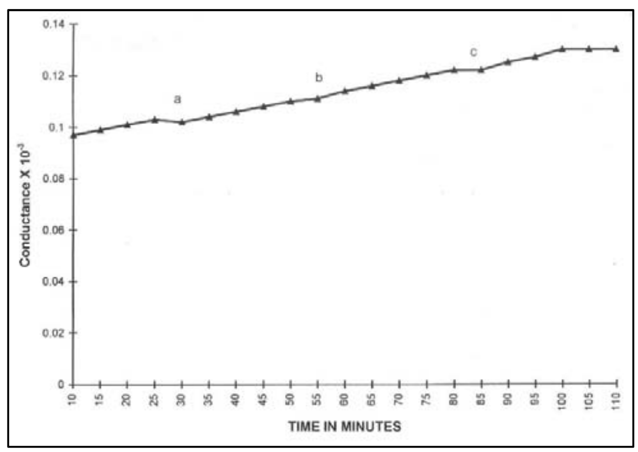

Fig 2: Decomposition of Mercury Peroxychromate prepared in Ethyl Acetate

Table2.1: Velocity Constants of different stages of decomposition calculated from the observation of table 2.1A

First Stage			Second Stage		
Time (Minute)	a-x (a=0.102)	K	Time (Minute)	a-x (a=0.111)	K
10	0.005	0.3016	35	0.007	0.07897
15	0.003	0.23513	40	0.005	0.077516
20	0.001	0.2312	45	0.003	0.08025
			50	0.001	0.09420

Third Stage			Fourth Stage		
Time (Minute)	a-x (a=0.122)	K	Time (Minute)	a-x (a=0.130)	K
55	0.011	0.04375	85	0.008	0.03280
60	0.008	0.04541	90	0.005	0.03620
65	0.006	0.04635	95	0.003	0.03968
70	0.004	0.04883			

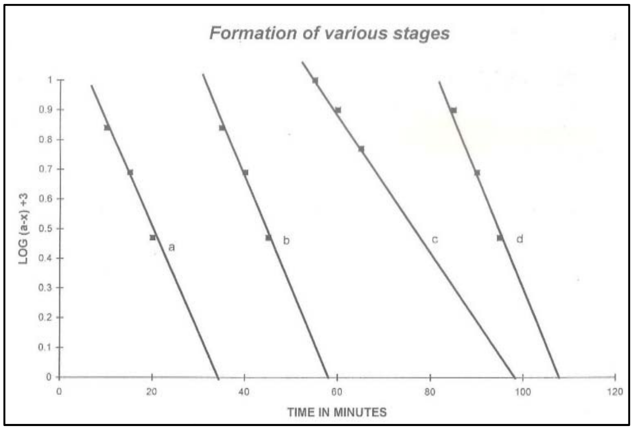

Fig 2A: Formation of various stages

3. Discussion

The conductometric investigations were carried out for mercury peroxychromate during its decomposition over conductivity water. The conductivity of water decomposition product at varying temperatures, with varying ratios of mercury peroxychromate and conductivity water was measured.

The graphs between conductivity vs time have been plotted. Three breaks are obtained in each plot. The starting point of the plot is the beginning of first stage and the first break is the beginning of the second stage and second break is the final point for the second stage of decomposition and so on. Thus the decomposition of mercury peroxychromate which contains $Cr_2O_{10}^{-2}$ ion may be represented through different stages as:-

$Cr_2\,O_{10}^{-2}$ —First Break→ $Cr_2O_9^{-2}$+ (O) ------ (i)

$Cr_2\,O_9^{-2}$ —Second Break→ $Cr_2O_8^{-2}$+ (O) ------ (ii)

$Cr_2\,O_8^{-2}$ —Third Break→ $Cr_2O_7^{-2}$ + (O) ------ (iii)

At the beginning of the fourth stage the color of solution is yellow due to $Cr_2O_7^{-2}$ion. To identify the presence of dichromate ion, it was titrated iodometrically.

By calculating the velocity constant for each stage (vide table-1A to 2A) the formation of different ions during decomposition of mercury peroxychromate in contact with conductivity water has been confirmed. The values of velocity constants for any particular stages are fairly constant but differ from any other stage. It shows that every stage is quite different from the other. Further to determine the order of reaction (decomposition) of each stage, the graphs between time vrs. log (a-x) were plotted. In each case a staright line was obtained showing that the decomposition of each stage is a reaction of first order.

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