International Journal of Chemical Studies

P-ISSN2349–8528
E-ISSN 2321–4902
IJCS 2015; 3(3): 26-28

Received: 25-08-2015
Accepted: 27-09-2015

Jaya Gupta
Department of Chemistry,
Agra College, Agra.

Amit Gupta
Department of Chemistry,
Agra College, Agra.

Kinetic studies of lead peroxychromate during its self-decomposition

Jaya Gupta, Amit Gupta

Abstract
To determine the nature of lead peroxychromate, the chemical kinetic study of self decomposition of lead peroxychromate was done. At a particular temperature, the value of velocity constants are fairly constant which suggests that decomposition of lead peroxychromate is of first order reaction. Calculation of free energy of activation suggests that free energy of activation remains constant and rate of reaction is independent of concentration.

Keywords: Lead peroxychromate, kinetic study, self-decomposition, order of reaction.

Introduction
Decomposing peroxychromate has been used as a source of active oxygen species to examine their effects on biochemical functions [1-2]. Decomposition of potassium peroxychromate produces hydroxyl radical that can peroxidize the unsaturated fatty acids of phospholipid dispersion [3]. The peroxychromate anion decomposes readily in aqueous systems to release several species capable of causing lipid peroxidation. These species are hydrogen peroxide, hydroxyl ion, singlet oxygen, superoxide radical. Singlet oxygen produced by decomposition of peroxychromate has been suggested as one of the primary lipid oxidants. 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 kinetically studied [4-10]. In the present work chemical kinetic studies of lead peroxychromate was done to assess the correct nature of lead peroxychromate.

Experimental
All the reagent used were of AR (Analytical Reagent) and GR (Guaranteed Reagent) grade. The sample of lead peroxychromate was washed thoroughly with ice cold water to remove the excess of hydrogen peroxide. This was then dried by freezing the water if any present in it and kept for study at 0 °C. For kinetic studies, a particular volume of lead peroxychromate was taken in a dry flask and kept in thermostat maintained at desired temperature. When the flask and its contents attained the temperature of bath the reaction was followed by determining the amount of lead peroxychromate remained undecomposed in ethyl acetate at different time intervals (at zero time, the titre value corresponds to the undecomposed lead peroxychromate). 5ml. of lead peroxychromate at zero time were pipette out in a flask which contain 20 ml. of ice cold water and 1ml. of 10% potassium iodide solution. The iodine liberated was titrated iodometrically against N/100 sodium thiosulphate solution using 10 ml. of $2N.H_2SO_4$ and starch as an indicator. After a definite time interval again 5ml of the reaction mixture was withdrawn from the same flask and titrated similarly as described above. This process was repeated, till whole of the lead peroxychromate was decomposed. (Table1, 2 and 3)

Jaya Gupta
Department of Chemistry,
Agra College, Agra.

Table 1: Self-Decomposition of Lead Peroxychromate

Lead Peroxychromate =5ml.
Temperature = 5 ºC

Time(Minutes)	Volume (ml.) of hypo solution used	Log(a-x)	K
0.0	7.4	0.8692	
7.5	7.2	0.8573	0.003653854
15.0	7.0	0.8450	0.003705324
22.5	6.7	0.8260	0.004417350
30.0	6.5	0.8129	0.004323373
37.5	6.4	0.8061	0.003872217
45.0	6.2	0.7923	0.003932501
52.5	6.1	0.7853	0.003680496
60.0	5.9	0.7708	0.003776141
67.5	5.8	0.7634	0.003609866
75.0	5.6	0.7481	0.003716849
82.5	Decomposed		
90.0	Decomposed		

Mean K_1= 0.003868788 equi. /min

Table 2: Self-decomposition of Lead Peroxychromate

Lead Peroxychromate = 5ml.
Temperature =15 ºC

Time(Minutes)	Volume (ml.) of hypo solution used	Log (a-x)	K
0.0	7.3	0.8633	
7.5	7.0	0.8450	0.005596234
15.0	6.5	0.8129	0.007739539
22.5	6.1	0.7853	0.007983019
30.0	5.7	0.7558	0.008248425
37.5	5.3	0.7242	0.008539339
45.0	5.0	0.6989	0.008411213
52.5	4.7	0.6720	0.008388403
60.0	4.4	0.6434	0.008439350
67.5	Decomposed		
75.0	Decomposed		

Mean K_2= 0.00791819 equi. /min

Table 3: Self-decomposition of Lead Peroxychromate

Lead Peroxychromate =5ml.
Temperature = 25 ºC

Time(Minutes)	Volume (ml.) of hypo solution used	Log (a-x)	K
0.0	6.7	0.8260	
7.5	5.9	0.7708	0.016957078
15.0	5.2	0.7160	0.016899638
22.5	4.5	0.6532	0.017693415
30.0	3.9	0.6020	0.018040949
37.5	3.6	0.5563	0.016567616
45.0	3.1	0.4913	0.017129873
60.0	2.7	0.4313	0.017314657
67.5	Decomposed		
75.0	Decomposed		

Mean K_3= 0.017229032 equi. /min

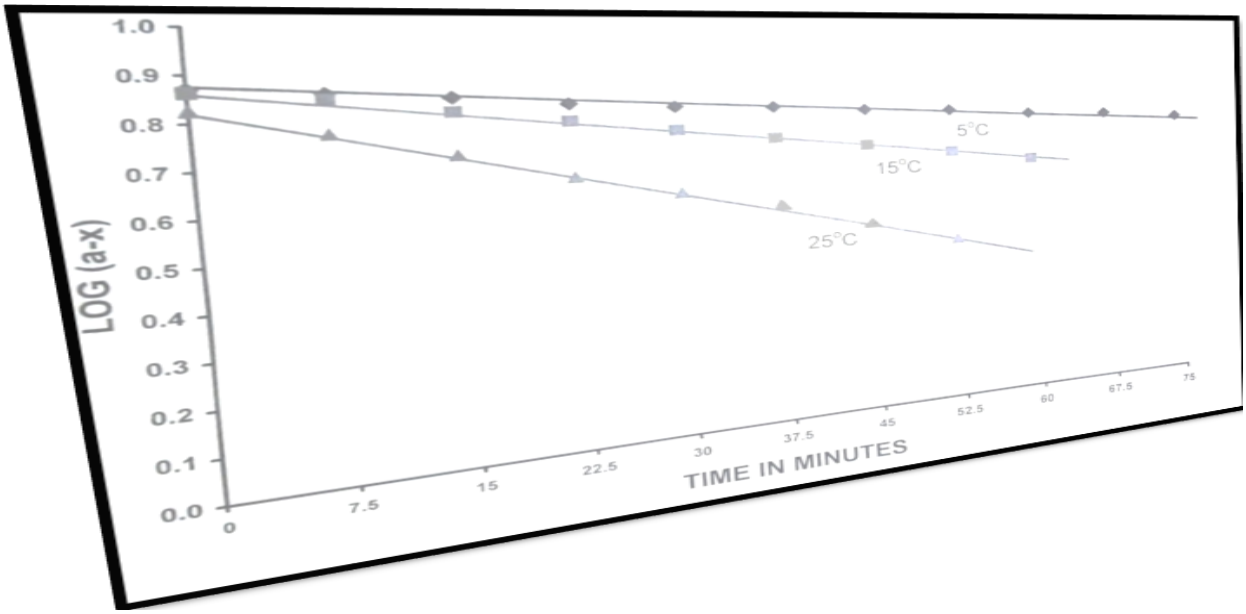

Fig 1: Kinetic study of self-decomposition of lead peroxychromate

Value of temperature coefficient of K' is 2.046684905 and K" is 2.175880094. Energy of activation of E_1 is 11.38Kcal/mole and E_2 is 13.24K Cal/mole. Mean energy of activation is 12.31Kcal/mole. The free energy of activation at 15 ºC is 3.3039 Kcal/mole and at 25 °C is 3.144Kcal/mole.

Result and Discussion

In this study, the velocity constants, temperature coefficients, energy of activation were calculated to arrive at definite conclusion regarding the constitution of lead peroxychromate. The values of velocity constant (Table 1 to 3) calculated with

the help of first order reaction are fairly constant showing the process of decomposition is a first order reaction. These values of temperature coefficients are quite close to the theoretical values K=2 to3 at 10 °C difference in temperature for a first order reaction. This further confirms the process of decomposition to be first order reaction. The graph between log (a-x) Vs time are straight lines which further support to the above fact.

The values of energy of activation E_1 and E_2 are found to be 11.38Kcal/mole and 13.24Kcal/mole respectively at temperature 15 °C and 25 °C with respect to temperature 5 °C. The mean value of energy of activation of lead peroxychromate during the decomposition comes to 12.31K Cal/mole. The value of E increases with rise in temperature.

On the basis of above calculation the decomposition of lead peroxychromate containing

$Cr_2O_{10}^{-2}$ ion is a unimolecular reaction.

$$Cr_2O_{10}^{-2} \xrightarrow{\text{Fast}} Cr_2O_8^{-2} + 2\,O \quad (1)$$

$$Cr_2O_8^{-2} \xrightarrow{\text{Fast}} Cr_2O_7^{-2} + O \quad (2)$$

The complete decomposition of lead peroxychromate may be represented as:

$$Pb\,(Cr_2O_{10})_2 \xrightarrow{\text{Fast}} Pb(Cr_2O_7)_2 + 6\,O \quad (3)$$

The free energy of activation (E_1 and E_2) confirms the idea that energy of activation remains constant and rate of reaction is independent of concentration.

Conclusion

Chemical kinetic study of self-decomposition lead peroxychromate shows that it is of first order and calculation of free energy of activation reveals that free energy of activation remains constant and rate of reaction is independent of concentration.

Acknowledgements

We thank to Dr. A.K. Gupta Chemistry Department, Agra College, Agra and Principal Agra College, Agra for providing necessary laboratory facilities and for full support.

References

1. Baird MB, Massie HR, Piekielniak MJ. Formation of lipid peroxides in isolated rat liver microsomes by singlet molecular oxygen. Chem Biol. Interact 1977; 16: 145-143.
2. Paschen W, Weser U. Problem concerning the biochemical action of superoxide dismustase Z.PhysicalChem1975; 356:727-737.
3. Edwards JColin, Peter JQuinn. Decomposing potassium peroxychromate produces hydroxyl radical (*OH) that can peroxidize the unsaturated fatty acids of phospholipid dispersions, Journal of Lipid Research.1982; 23:994-100.
4. Zhang L, Lay Pa. EPR spectroscopic studies on the formation of chromium (V) peroxo complexes in reaction of chromium (VI) with hydrogen peroxide. Inorg Chemistry 1998; 37:1729-1733.
5. Griend DAV, Golden JS, Arrington CA(Jr). Kinetics and mechanism of chromate reduction with hydrogen peroxide in base. Inorg Chemistry 2002; 41:7042-7048.
6. Perz-Benito JF, Arias C A. Kinetic study of the chromium VI– hydrogen peroxide reaction. Role of the diperoxochromate (VI) intermediates, J PhysChem. 1997; 101:4726-4733.
7. Witt SN, Hayes DM. Kinetic and mechanism of the formation of violet-peroxychromate in aq. solution Inorg Chemistry 1982; 21:4014-4016.
8. Gupta AK, Gupta Amit, Gupta Jaya. pH Metric studies of lead peroxychromate during its decomposition over water. Oriental Journal of Chemistry.2006*;* 22(2): 421-422.
9. Gupta Jaya, Gupta Amit, Gupta AK. Determination of oxidizing powers of lead peroxychromate and its water decomposition product. J Chemtracks. 2007; 9(1&2):147-150.
10. Gupta AK, Gupta Amit, Gupta Jaya. Colorimetric study of dynamic formation of lead IV peroxychromate. Acta Ciencia Indica 2007; 33C (1):17-22.