NOTE

Kinetics of the Thermal Decomposition of Oxalic Acid Dihydrate adsorbed on Charcoal

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Thermal decomposition of oxalic acid dihydrate was studied
from a kinetic view point. This was done in the adsorbed condition
on charcoal and in the presence of various additive combinations
of the two by the method of dynamic TGA. In the adsorbed state
and in presence of high concentrations of charcoal as additive,
significant rate enhancement for the thermal decomposition of the
acid was observed.

The thermal decomposition of oxalic acid dihydrate is reported in the literature[1, 2]. However no report is available on aspects of catalysis and kinetics etc. The decomposition occurs as a two stage process, the first stage involving the elimination of the two molecules of water of hydration and the second stage consisting of the elimination of CO, CO_2 and H_2O. The effect of adsorption on the thermal decomposition has been investigated from the kinetic point of view.

A preliminary adsorption study of oxalic acid dihydrate was carried out using BDH AnalaR grade chemicals, employing standard titrimetric procedures. The adsorbed smaple with 20% w/w of acid dihydrate is used for TG study. Other additive samples are prepared in various proportions (Table-1) taking scrupulous care. The TG traces of all the samples are recorded using Dupont 2000 thermobalance in nitrogen atomsphere at a heating rate of 10 K min^{-1}.

The kinetic parameters were calculated from the mass loss data obtained from TG traces, by using mechanism non-invoking equations. The methods employed are Coats-Redfern (CR)[3], Horowitz-Metzger (HM)[4] and Freeman-Carroll (FC)[5]. The various kinetic parameters such as E, Z and ΔS^* were calculated for the different samples using the above methods. These are given in Table-1.

The TG trace of pure oxalic acid dihydrate has indicated two stages as expected, with the activation parameters as given in Table-1. However quite interestingly for the sample with 20% w/w of the acid dihydrate adsorbed on charocoal decomposition occurs as a single stage. The activation energy E, frequency factor Z and the entropy of activation ΔS^* show decrements indicating a definite catalytic effecton decomposition consequent to adsoption. An intimately

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TABLE-1
VARIOUS KINETIC PARAMETERS OF OXALIC ACID DIHYDRATE ADSORBED ON CHARCOL

Sample	T_i	T_f	T_s	E (kJ mole^{-1})			Z (Sec^{-1})			ΔS^* (J mole^{-1} K^{-1})		
				CR	HM	FC	CR	HM	FC	CR	HM	FC
Oxalic acid (blank)												
I stage	333.0	425.0	349.7	60.8	56.0	50.2	3.9×10^5	2.2×10^6	3×10^4	-138.9	-124.6	-160.3
II stage	438.0	506.0	499.6	108.0	130.1	97.2	1.5×10^9	4.4×10^{11}	2.4×10^3	-73.7	-26.3	-88.8
Oxalic acid (20%) (Adsorbed)												
+ C (88%) w/w	392.0	454.5	438.5	124.5	139.5	106.1	5.4×10^{12}	6.4×10^{13}	6.5×10^{10}	-4.4	16.2	-41.1
Oxalic acid (20%)												
+ C (80%) w/w	392.0	460.0	420.0	135.7	138.1	123.5	9.6×10^{13}	2.5×10^{14}	6.6×10^{12}	19.9	27.8	-2.3
Oxalic acid (40%)												
+ C (60%) w/w	397.5	465.5	450.4	143.3	163.4	131.9	3.5×10^{14}	1.6×10^{16}	3.0×10^{13}	30.1	61.6	9.5
Oxalic acid (80%)												
+ C (20%) w/w												
I stage	311.0	363.6	348.5	75.0	85.8	81.0	1.4×10^9	1.1×10^{10}	3.3×10^{10}	-71.1	-54.0	-44.8
II stage	371.0	499.4	439.0	78.8	88.3	79.6	5.5×10^6	3.1×10^7	1.6×10^7	-119.0	-104.6	-109.9

homogenised mixture of the acid dihydrate and charcoal in the same proportion (20% w/w) also has a similar kinetic behaviour. This points to the possibility of some phenomenon akin to adsorption taking place in the solid state itself by intimate mixing. The fact that a loose combination of the acid dihydrate and charcoal in the same proportion has give a TG trace exactly identical to that of the pure compound, ruled out the possibility of a chemical effect due to carbon.

With higher proportions of the acid dihydrate in the additive simples the catalytic effect seems to wear off. This is evident from the decomposition pattern of the sample with 80% w/w of the acid dihydrate where the two stage process is restored. The kinetic parameters are also nearly identical to those of the pure compound.

REFERENCES

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