

Effect of Impurities on Thermal Decomposition of Calcium Carbonate

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Calcium carbonate, in the aragonite form, undergoes an irreversible transformation to calcite form around 520°. Pure aragonite has been doped with cationic impurities like Na⁺, Mg²⁺, Zn²⁺, Y³⁺ in various atomic percentages and effect of the impurities on the kinetics and energetics of the thermal decomposition of pure calcium carbonate studied. By employing DTA technique, the enthalpy, energy of activation and the order of reaction for the decomposition reaction have been calculated.

THE kinetics of thermal decomposition of pure calcium carbonate has been examined by several workers¹⁻⁴, but there is very little information⁵ in the literature on the effect of impurities on enthalpy, kinetics and energetics of its decomposition. Such a study is of particular importance to explain the role of impurities in lime burning. Besides this, the data on thermal decomposition will be of great interest as the substance is one of the few well-defined carbonates. Furthermore, most of the earlier reported data on aragonite are on samples containing unknown amounts of different impurities⁶⁻⁸.

In the present investigation the kinetics of decomposition of calcium carbonate in the presence of known amounts of different impurity cations has been studied. The impurity cations (Na⁺, Mg²⁺, Zn²⁺, Y³⁺) were chosen on the basis of their ionic size and doped in aragonite in different atomic percentages. The values for enthalpy of decomposition (ΔH), energy of activation (E_a) and order of the reaction (n) for different impurity doped samples of calcium carbonate have been evaluated from DTA data.

Aragonite samples were prepared by a known procedure⁹ based on the hydrolysis of trichloroacetate salts. For the preparation of doped samples known amounts of impurity cations were taken in the form of carbonates or oxides along with the sample of pure calcium carbonate before reacting with trichloroacetic acid. All the chemicals used were of AR grade.

The DTA studies were carried out employing a Fisher thermoanalyser, model 260, fitted with an automatic voltage stabilizer, recorder and an amplifier. The curves were recorded with a constant heating rate of 10°/min, under controlled conditions (packing, particle size, etc.). Calcined α -alumina was used as a reference material. The activation energy was calculated following the method of Borchardt and Daniels¹⁰. ΔH value was computed by comparing the area of decomposition peak for the doped calcium carbonate sample with that of pure calcium carbonate. The order of the reaction for the pure and doped samples was determined by employing Kissinger's method¹¹.

The ΔH values estimated from the peak areas may have an uncertainty of $\pm 5\%$. The activation energy values obtained by employing the procedure of Borchardt and Daniels may have large uncertainties ($\sim \pm 15\%$). However, the comparison of the values in related systems is valid.

The temperature at the start of the decomposition peak (T_i), decomposition temperature T_d (peak temperature), ΔH and E_a values and the order of the reaction for the pure and various doped samples are listed in Table 1.

It is apparent from Table 1 that incorporation of impurities affects T_i , T_d , ΔH and E_a values. The activation energy value of 44 kcal/mole and the order of reaction (0.85) for the pure calcite agree well with the earlier reported data^{4,12-14}. The ΔH values for the various doped samples range from 27.6 to 57.4 kcal/mole compared to 40 kcal/mole for the pure calcite. The variation in the values of activation energy is also fairly large, ranging from 44 kcal/mole for the pure to 200 kcal/mole for the doped samples. The decomposition temperature and the initial temperature of the peak are also markedly affected by cation impurities.

The increase in Na⁺ impurity in calcite increases both ΔH and E_a values; T_d values do not show any regular trend. With the increase in Mg²⁺ impurity, from 0.01 to 1.5 atomic per cent, the ΔH values increase. For Zn²⁺ doped calcium carbonate samples, the ΔH values first increase with the increase in zinc content up to 0.5% and

TABLE 1 — VALUES OF ENTHALPY OF REACTION (ΔH), DECOMPOSITION TEMPERATURE (T_d), INITIAL TEMPERATURE OF THE PEAK (T_i), ENERGY OF ACTIVATION (E_a) AND ORDER OF REACTION (n) FOR CALCIUM CARBONATE CONTAINING DIFFERENT IMPURITIES

Impurity (atom %)	ΔH^* (kcal/mole)	n	E_a (kcal/mole)	T_d (°C)	T_i (°C)
None	40.0	0.85	44	970	850
Mg ²⁺ (0.01)	41.6	0.69	157	971	889
Mg ²⁺ (0.1)	41.9	0.71	110	972	855
Mg ²⁺ (0.5)	49.6	0.79	80	981	845
Mg ²⁺ (1.0)	50.0	0.86	86	984	808
Mg ²⁺ (1.5)	55.4	1.04	111	994	868
Zn ²⁺ (0.01)	52.7	0.71	140	961	838
Zn ²⁺ (0.1)	54.7	0.75	128	962	825
Zn ²⁺ (0.5)	55.9	0.86	127	966	822
Zn ²⁺ (1.0)	48.7	0.85	135	962	832
Zn ²⁺ (1.5)	46.1	0.75	197	961	855
Na ⁺ (0.01)	41.8	0.75	123	980	855
Na ⁺ (0.1)	41.9	0.74	131	980	855
Na ⁺ (0.5)	42.4	1.00	137	964	839
Na ⁺ (1.0)	44.3	0.96	155	956	834
Na ⁺ (1.5)	51.7	0.95	165	981	860
Na ⁺ (5.0)	51.8	0.92	194	961	873
Y ³⁺ (0.01)	57.4	1.09	125	989	855
Y ³⁺ (0.1)	56.8	0.80	91	987	830
Y ³⁺ (0.5)	51.2	0.88	144	976	854
Y ³⁺ (1.0)	31.3	0.77	200	968	882
Y ³⁺ (1.5)	36.9	0.69	176	987	886
La ³⁺ (0.5)	29.8	0.95	62	961	798
Nd ³⁺ (0.5)	27.6	0.85	91	964	810

* ΔH for the reaction $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$ is taken as standard. Ionic radii of Ca²⁺, Mg²⁺, Zn²⁺, Na⁺, Y³⁺, La³⁺ and Nd³⁺ are 0.099, 0.065, 0.074, 0.095, 0.093, 0.115 and 0.108 nm respectively.

thereafter start decreasing. For both Zn^{2+} and Mg^{2+} doped samples E_a values first decrease up to 0.5% impurity and then start increasing. The decomposition temperatures increase regularly in the case of Mg^{2+} doped samples but remain unaffected with the increase in Zn^{2+} content. With the increase in Y^{3+} content, ΔH generally decreases while the E_a values do not show any regular pattern. The decomposition temperatures follow the same trend as ΔH values. The values for the order of reaction determined from DTA curves range from 0.69 to 1.09 for the various doped samples. With the relative uncertainties in the determination of this quantity, one can take the order of reaction to be one.

A perusal of the data (Table 1) shows that as the E_a values increase, the starting point of the peak also shifts to higher temperatures; and with increase in ΔH values the peak temperatures increase.

From the above discussion it is clear that both, ΔH values and E_a values and T_d , T_i for the decomposition of calcium carbonate show marked variations for different cationic impurities.

The variation of T_d , T_i and E_a of decomposition with varying impurities is understandable, but there is no reason why the ΔH values should vary with impurities. It seems likely that the lower ΔH values may be because of the fact that decomposition occurs over wider temperature ranges causing broad and shallow DTA peaks. Accordingly, the ΔH values are low when the T_i and T_d values are low.

The present findings reveal that Na^+ and Y^{3+} impurities, when doped in aragonite, affect the decomposition characteristics of calcium carbonate differently in spite of the similar ionic sizes of the impurities. The difference in behaviour may be attributed to their different oxidation states and electronic configurations. This may possibly arise from the cation and anion vacancies produced by the $1+$ and $3+$ ions, but these effects are difficult to assess from the present study. It is also observed that if the valency states of the dopents are the same but the ionic radii are different e.g. Mg^{2+} and Zn^{2+} , the behaviour of the doped samples is similar up to a certain percentage of the impurity.

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Electric Dipole Moment of Some New Triphenyltin(IV) N,N-Disubstituted Dithiocarbamates

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The electric dipole moment of several new triphenyltin(IV) dithiocarbamates of the general formula $Ph_3Sn(IV)SCSNR_2$ (where $SCSNR_2 = dtc = n$ -butyl-, benzyl-, phenyl-, dimethyl-, dibutyl-dithiocarbamates; and morpholine- and piperidine-N-carbodithioate) have been calculated from Guggenheim method. The dipole moment is found to decrease with an increase in the electron releasing ability of the NR_2 group. The results indicate an ester type structure of the compounds having unidentate dithiocarbamate group.

SEVERAL workers¹⁻⁴ have suggested that heavy metal dithiocarbamates possess electric moment which are close to the value expected for a symmetrical chelate arrangement of the dithiocarbamate group around the metal atom. Recently Bonati *et al.*⁵ determined the dipole moment of some triorganotin(IV) and diorganotin(IV) dithiocarbamates and suggested a bidentate character of the dithiocarbamate group in $R_2Sn(IV)$ derivatives while for the corresponding $R_3Sn(IV)$ compounds, definite evidence for or against the chelating nature of the dithiocarbamate moiety was lacking.

In the present investigation, we report the dipole moment of seven triphenyltin(IV) dithiocarbamates of the general formula $Ph_3Sn(IV)SCSNR_2$ (where $SCSNR_2 = dtc = n$ -butyl-, benzyl-, phenyl-, dimethyl-, dibutyl-dithiocarbamate, morpholine- and piperidine-N-carbodithioate). The results indicate that the dithiocarbamate group is unidentate and molecular moment decreases with an increase in the electron releasing ability of the NR_2 group.

Triphenyltin(IV) dithiocarbamates were prepared and characterized as reported earlier⁶. The solutions were prepared in thiophene-free benzene which was distilled over anhydrous calcium chloride before use.

The electric dipole moment were calculated by Eq. (1), using a variation of the refractivity method outlined by Guggenheim⁷.

$$2 = \frac{9K7}{4\pi n} \cdot \frac{3}{(E_1+2)(\eta_1^2+2)} \cdot \left(\frac{\Delta}{C}\right)_{C \rightarrow 0} \\ = (E_{12} - \eta_{12}^2) - (E_1 - \eta_1^2) \quad \dots (1)$$

where C is concentration in mole per ml, E_1 and E_{12} are the dielectric constants for the solvent