Chapter III

Results and Discussion

Part (A)

Kinetics of Non-Isothermal Decomposition

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Part (A)

III-A. Kinetics of Non-Isothermal Decomposition:

Kinetic studies of the dynamic TG curves, at heating rates 2,3,5 and 10 K/min, for the dehydration of Co-nicotinate, Ni-nicotinate, Zn-nicotinate, Co-Ni-nicotinate, Co-isonicotinate, Ni-isonicotinate, Cu-isonicotinate and Co-Ni-isonicotinate were carried out and investigated according to of the different models of heterogeneous solid state reaction shown in Table(I-1). Three integral dynamic methods due to Coats-Redfern [22], Ozawa [23] and composite methods [25] were used to make the kinetic analysis. The kinetic parameters were calculated and discussed.

Figs.(III-A-(1-3)) shows representative weight changes as a function of temperature obtained from the dynamic measurements of thermal dehydration of the samples investigated. The compounds of $Cu(nic)_2.0.5H_2O$ and $Zn(isonic)_2.0.5H_2O$ aren't investigated because the water molecules are attached to the complex compounds through hydrogen bonding. And we are concentrated here on the other compounds in which the water molecules attached directly to the metal ions.

For each compound investigated the composite methods[25] gave equivalent curves and identical values for the kinetic parameters and showed that the dehydration step for each compound is described by any one of phase boundary (R_2 and R_3), Avrami-Erofeev random nucleation (A_2) and first order (F_1) models. The other models gave less satisfactory fit to the experimental data and (E_1) model gave the least fitting results as can be shown from Tables

(III-A-1,2). Figs.(III-A-(4-11)) show the results of data analysis performed according to composite methods of analysis for dehydration steps assuming (R_2) and (E_1) models. According to the phase boundry mechanism R_2, it is assumed that the nucleation step occurs instantaneously, so that the surface of each particles covered with a layer of product nucleation of dehydrated molecule, however may be a random process, not followed by rapid surface growth. As nuclei grow larger they may eventually impinge on one another. The values of kinetic parameters were calculated assuming (R_2) model, and tabulated in Tables (III-A-3).

The kinetic parameters were also calculated according to Coats - redfern and Ozawa methods, assuming (R_2) model for each compound investigated and the results were tabulated in Table (III-A-3). Figs (III-A-(12-17)), show the graphical representation of data according to both Coats-Redfern and Ozawa methods, assuming (R_2) model.

The results obtained from Table (III-A-3) show that, both composite methods of analysis gave identical values for kinetic parameters with less standard deviation. These results agree with those obtained from Coats-Redfern method and differ to some extent with that obtained by Ozawa in which the kinetic parameters calculated at different weight changes during dynamic measurements showed different results. This is possibly due to the variation of reaction mechanism with the fraction reacted.

The kinetic parameters calculated according to R_3 model which gave the best fit to experimental data other than (R_2) model are also tabulated in table (III-A-4). The results obtained for Coats-Redfern and Ozawa methods are the average results.

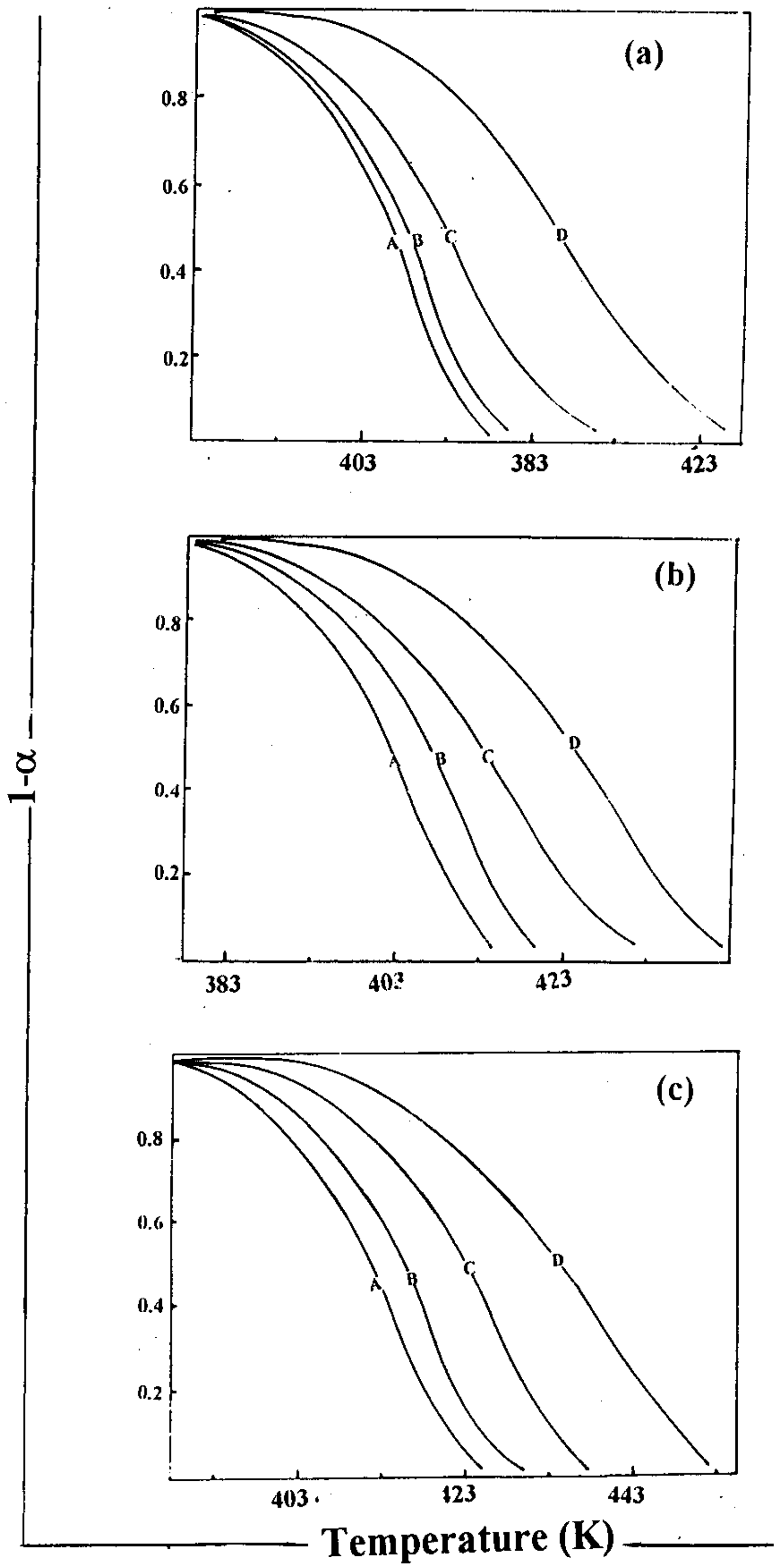

Fig.(III-A-1): Dynamic measurements for the thermal dehydration of: (a) cobalt nicotinate, (b) nickel nicotinate and (c) cobalt-nickel nicotinate. Heating rate: A;10, B;5, C;3 and D;2 K/min

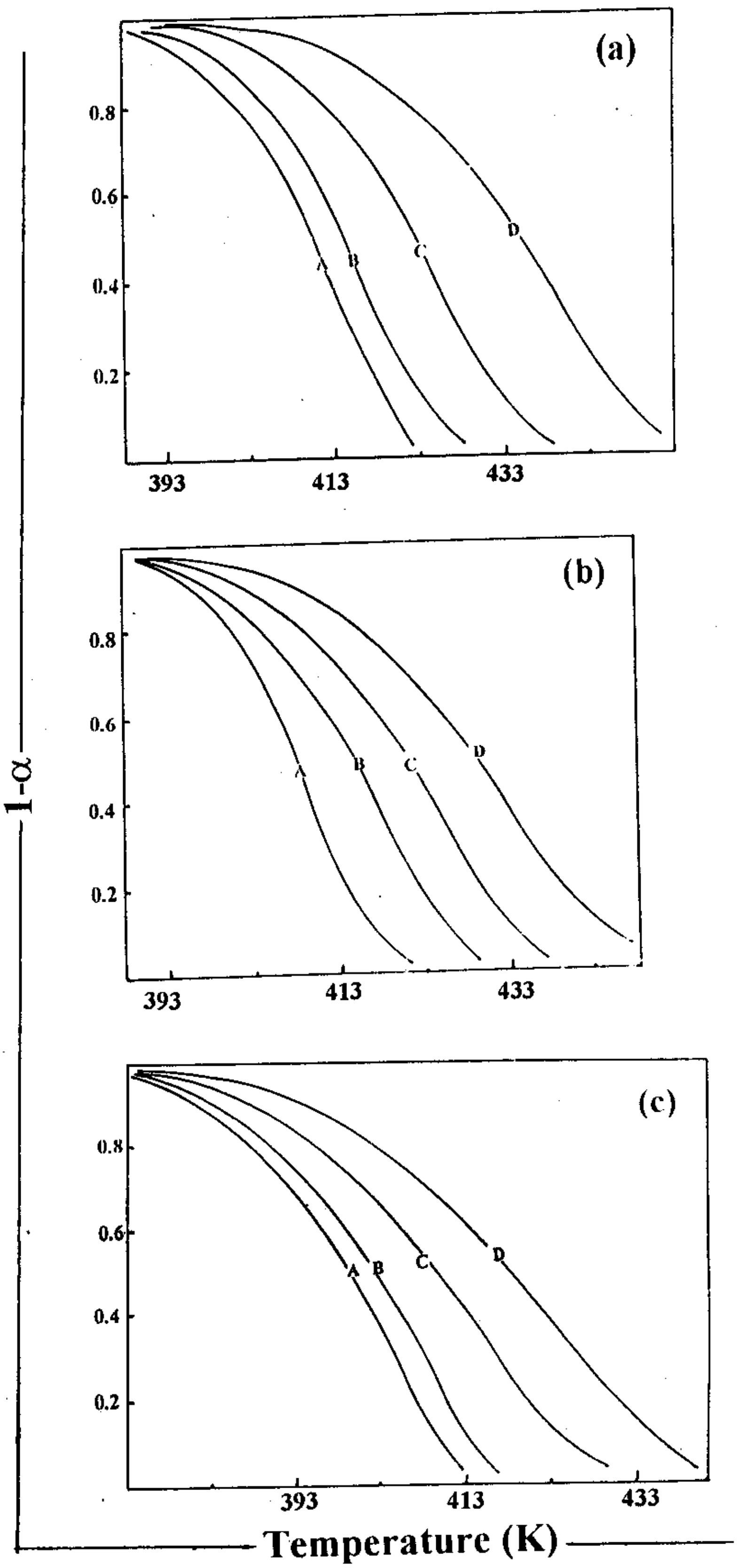

Fig.(III-A-2): Dynamic measurements for the thermal dehydration of: (a) cobalt isonicotinate, (b) nickel isonicotinate and (c) cobalt-nickel isonicotinate. Heating rate: A;10, B;5, C;3 and D;2 K/min

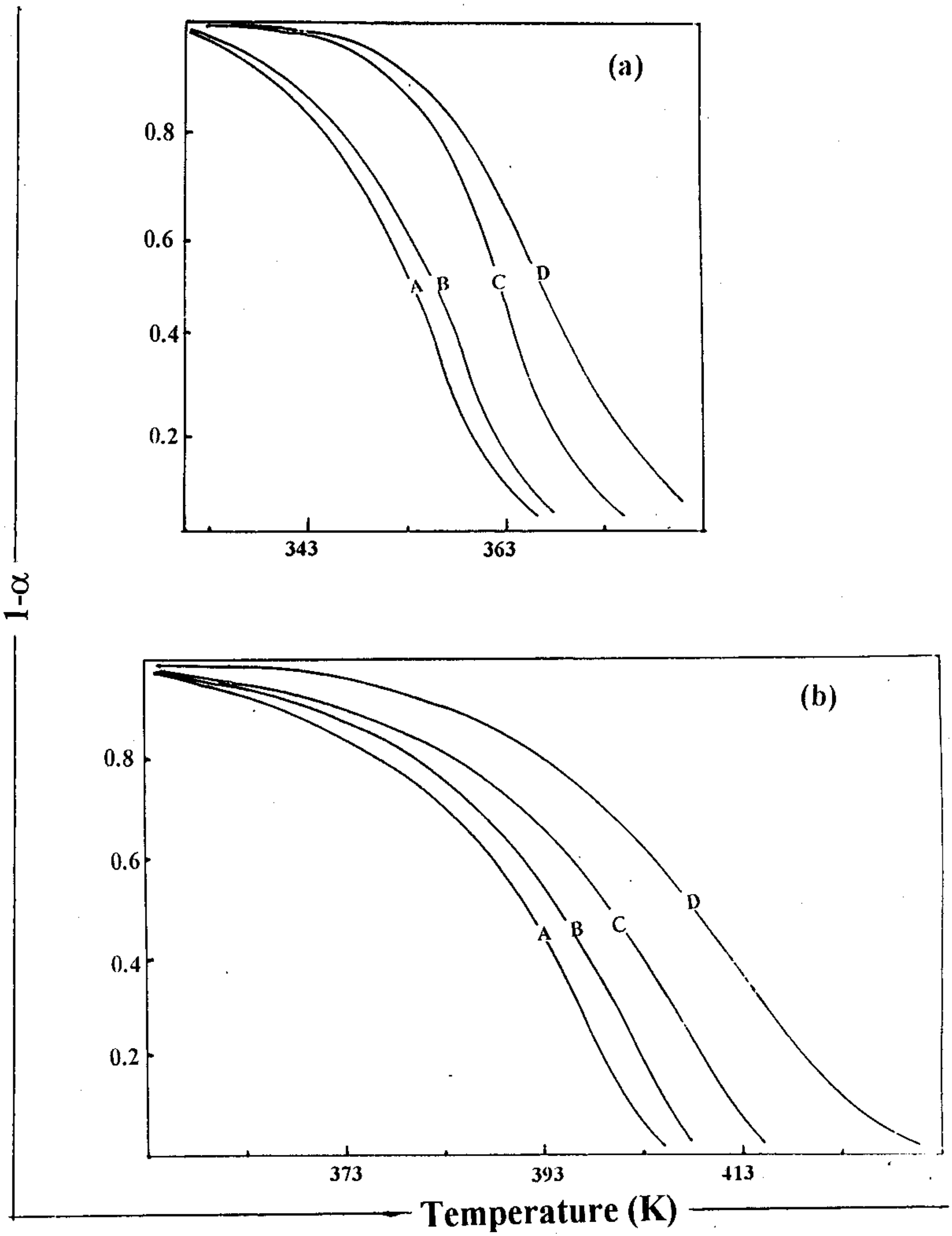

Fig.(III-A-3): Dynamic measurements for the thermal dehydration of: (a) zinc nicotinate and (b) cupper isonicotinate. Heating rate: A;10, B;5, C;3 and D;2 K/min

Table(III-A-1): correlation coefficients for the various kinetic models used in analysis assuming composite method(I).

Compounds	Correlation Coeff.														
	R_2	R_3	E_1	B_1	F_1	F_2	F_3	D_1	D_2	D_3	D_4	D_5	A_2	A_3	A_4
Cobalt nicotinate	0.965	0.958	0.551	0.085	0.959	0.854	0.346	0.893	0.897	0.901	0.899	0.901	0.957	0.889	0.801
Nickal nicotinate	0.979	0.978	0.558	0.363	0.980	0.859	0.852	0.925	0.928	0.930	0.929	0.927	0.973	0.895	0.809
Cobalt isonicotinate	0.987	0.986	0.556	0.370	0.986	0.859	0.862	0.952	0.952	0.950	0.952	0.939	0.933	0.826	0.733
Cobalt Nickal nicotinate	0.991	0.989	0.584	0.403	0.991	0.803	0.810	0.960	0.962	0.962	0.963	0.949	0.913	0.775	0.659
Zinc nicotinate	0.963	0.957	0.515	0.180	0.957	0.893	0.860	0.883	0.887	0.891	0.889	0.888	0.955	0.881	0.792
Nickal isonicotinate	0.984	0.970	0.505	0.058	0.965	0.871	0.815	0.900	0.900	0.899	0.900	0.892	0.971	0.916	0.836
Cupper isonicotinate	0.991	0.990	0.613	0.212	0.990	0.771	0.801	0.986	0.985	0.981	0.984	0.965	0.901	0.770	0.661
Cobalt Nickal isonicotinate	0.975	0.973	0.506	0.143	0.970	0.827	0.813	0.904	0.905	0.905	0.905	0.896	0.973	0.881	0.778

Table (III-A-2): correlation coefficients for the various kinetic models used in analysis assuming composite method(II).

Compounds	Correlation Coeff.													
	R_2	R_3	E_1	B_1	F_1	F_2	F_3	D_1	D_2	D_3	D_4	D_5	A_2	A_3	A_4
Cobalt nicotinate	0.970	0.962	0.517	0.027	0.962	0.872	0.857	0.899	0.902	0.905	0.904	0.905	0.961	0.908	0.837
Nickal nicotinate	0.982	0.981	0.521	0.338	0.981	0.877	0.863	0.929	0.932	0.934	0.933	0.930	0.978	0.914	0.845
Cobalt isonicotinate	0.988	0.987	0.521	0.339	0.987	0.875	0.871	0.955	0.955	0.953	0.955	0.942	0.943	0.855	0.778
Cobalt Nical nicotinate	0.992	0.991	0.551	0.365	0.992	0.828	0.823	0.963	0.965	0.965	0.965	0.951	0.927	0.816	0.721
Zinc nicotinate	0.967	0.960	0.489	0.161	0.960	0.903	0.867	0.888	0.892	0.895	0.893	0.892	0.958	0.897	0.821
Nickal isonicotinate	0.986	0.973	0.469	0.003	0.969	0.887	0.856	0.905	0.905	0.904	0.905	0.897	0.974	0.931	0.866
Cupper isonicotinate	0.992	0.991	0.572	0.145	0.991	0.804	0.818	0.987	0.986	0.983	0.985	0.967	0.919	0.816	0.731
Cobalt Nickal isonicotinate	0.979	0.976	0.472	0.093	0.973	0.849	0.827	0.909	0.910	0.909	0.910	0.901	0.976	0.902	0.818

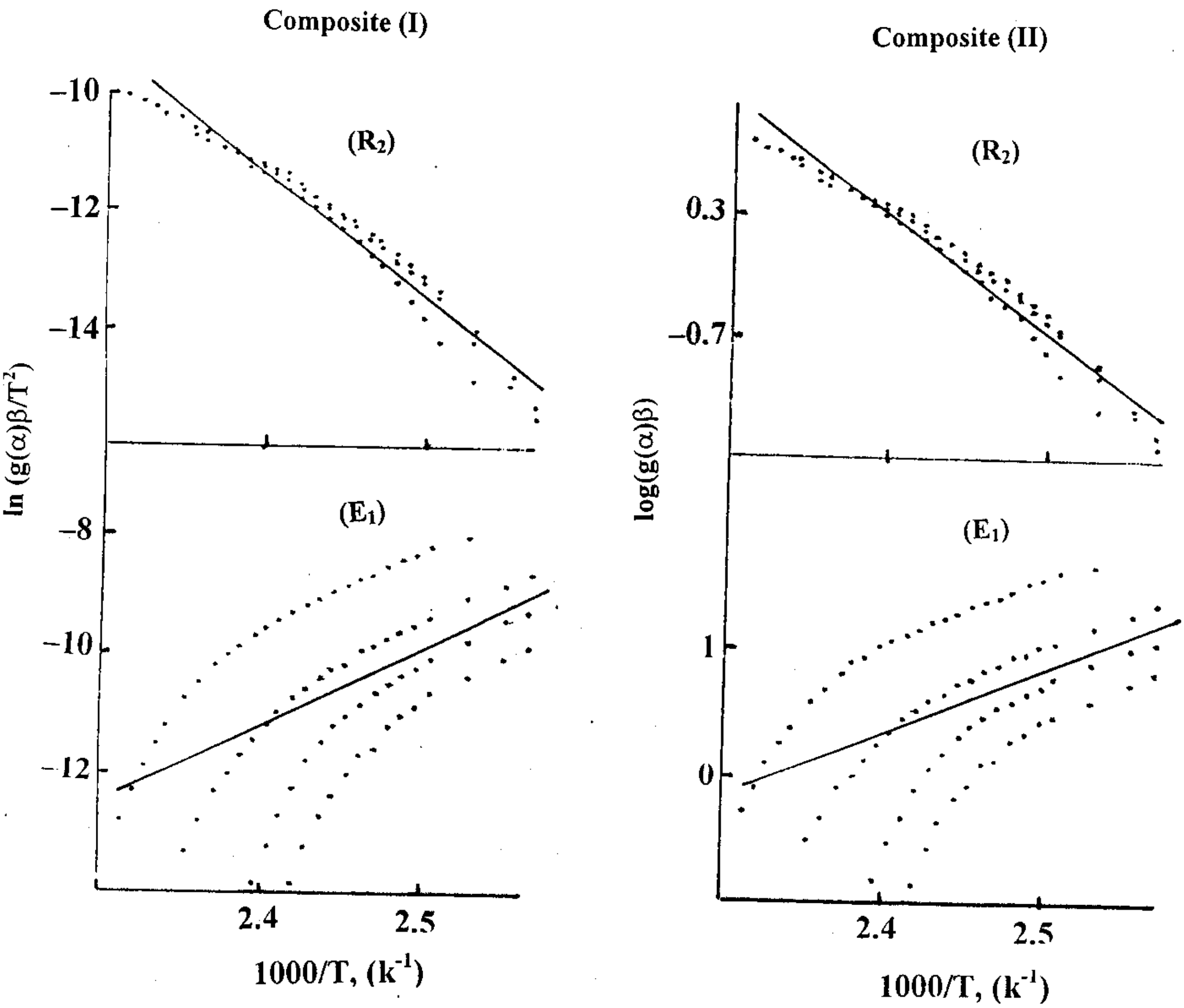

Fig.(III-A-4): Composite analysis of dynamic TG data of thermal dehydration of cobalt nicotinate, assuming (R_2) and (E_1) models.

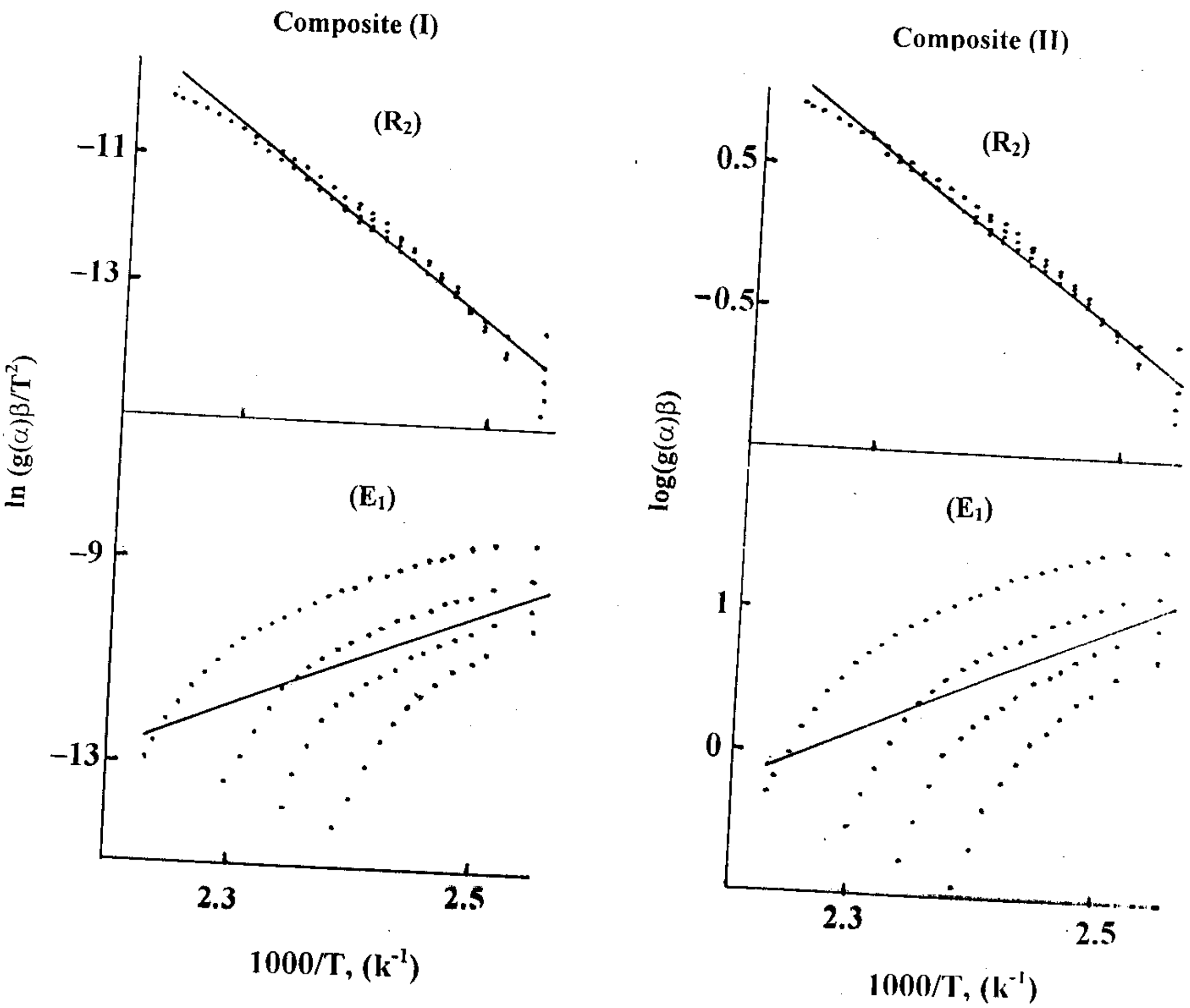

Fig.(III-A-5): Composite analysis of dynamic TG data of thermal dehydration of nickel nicotinate, assuming (R_2) and (E_1) models.

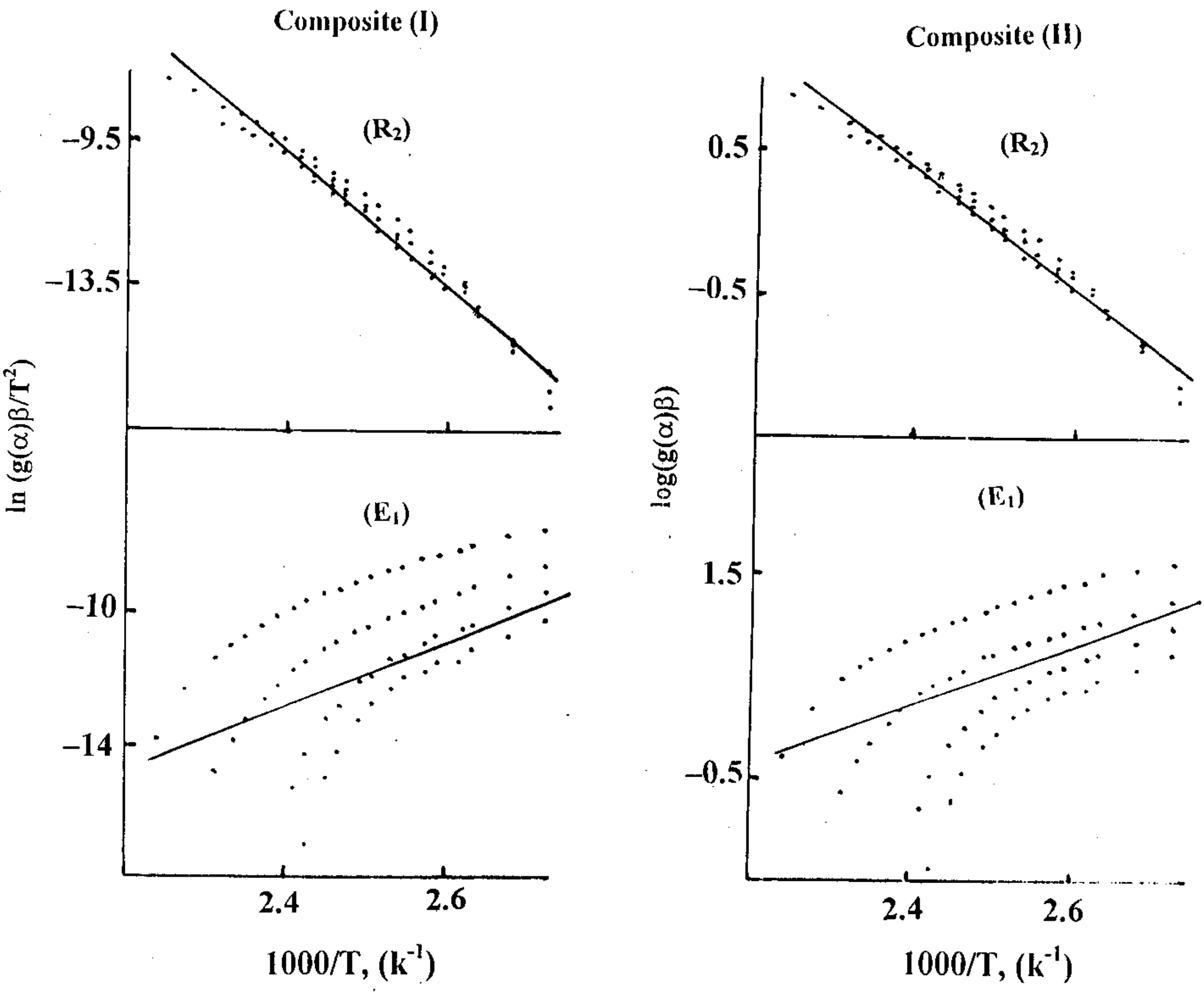

Fig.(III-A-6): Composite analysis of dynamic TG data of thermal dehydration of cobalt-nickel nicotinate, assuming (R_2) and (E_1) models.

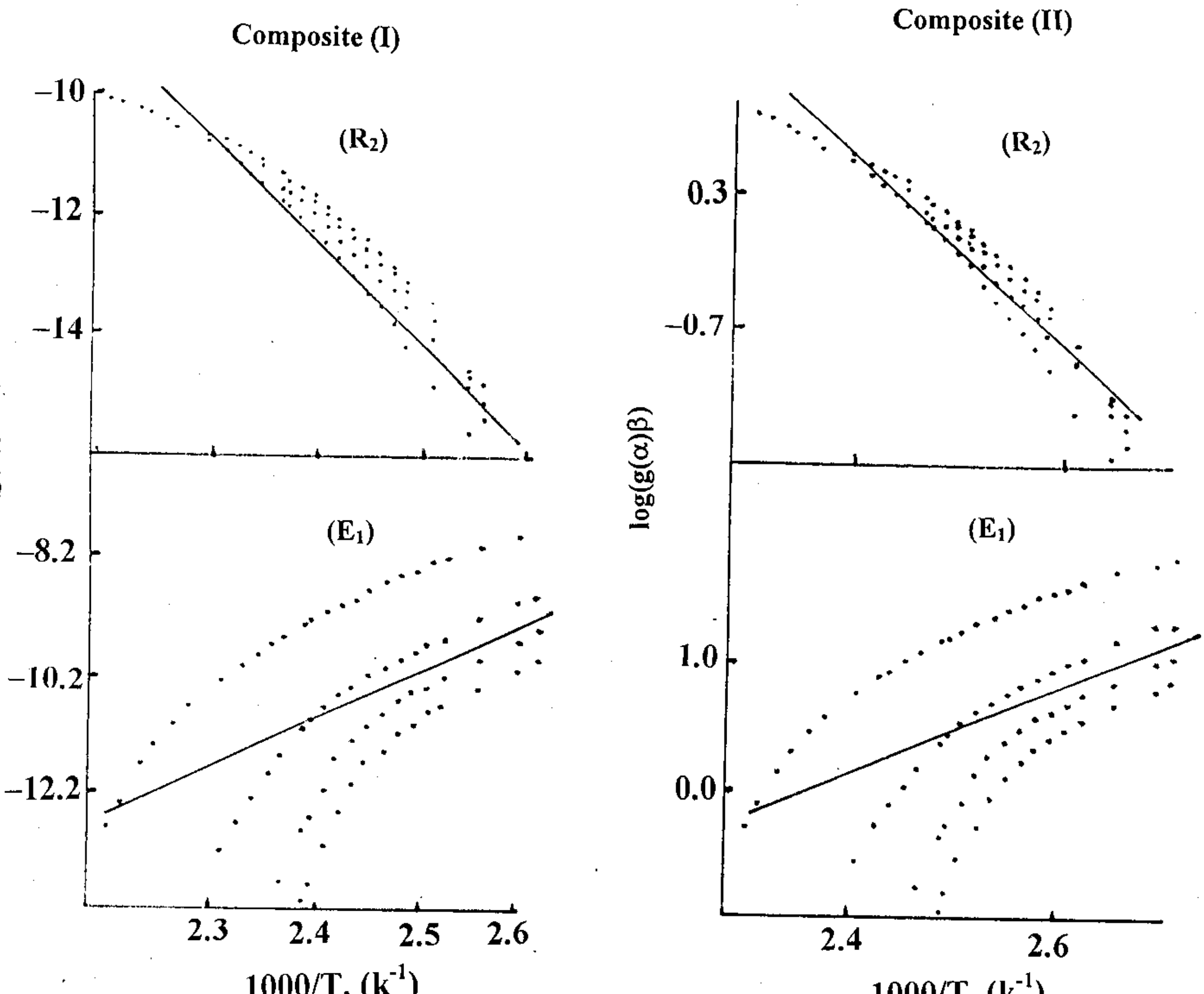

Fig.(III-A-7): Composite analysis of dynamic TG data of thermal dehydration of cobalt isonicotinate, assuming (R_2) and (E_1) models.

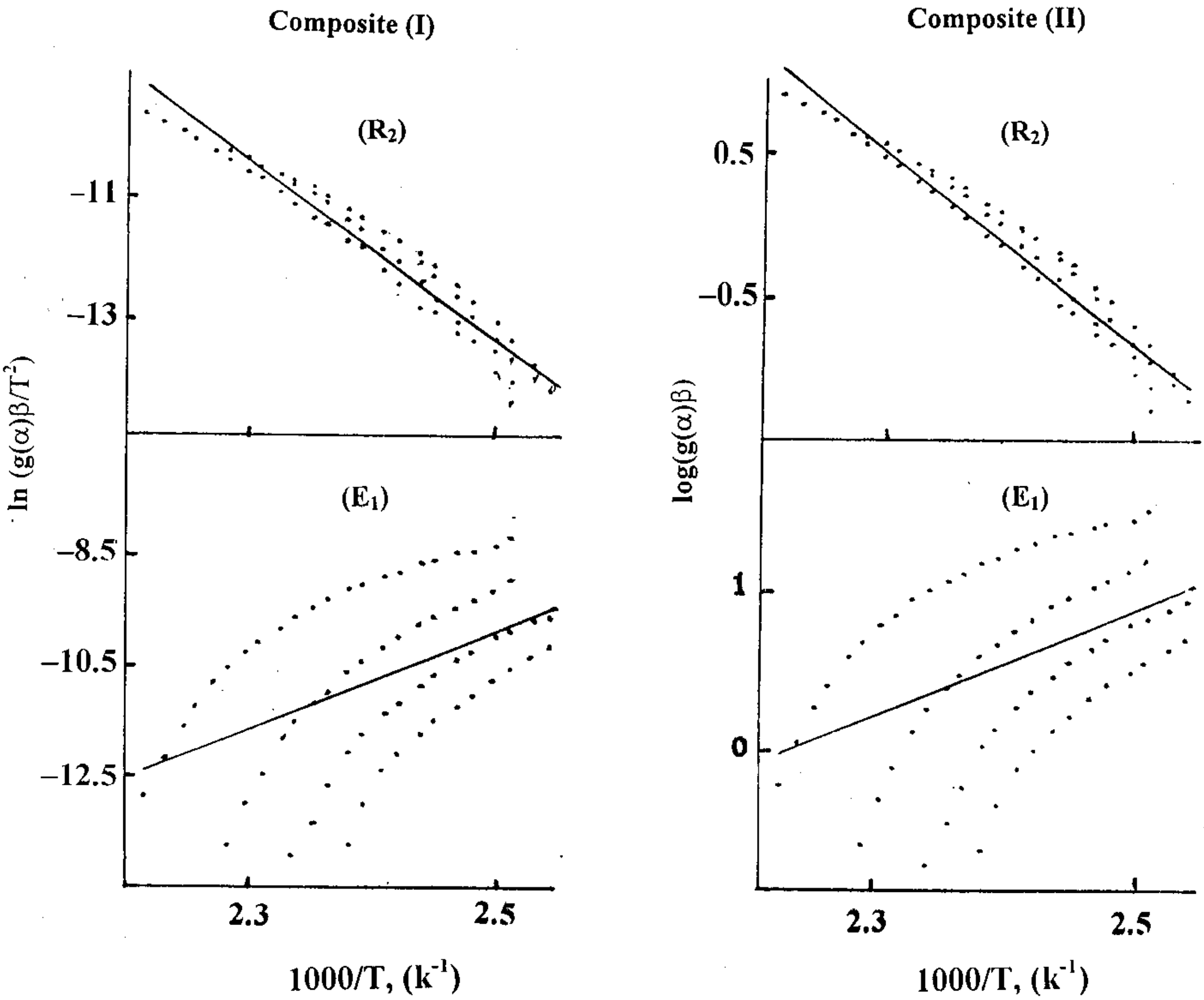

Fig.(III-A-8): Composite analysis of dynamic TG data of thermal dehydration of nickel isonicotinate, assuming (R_2) and (E_1) models.

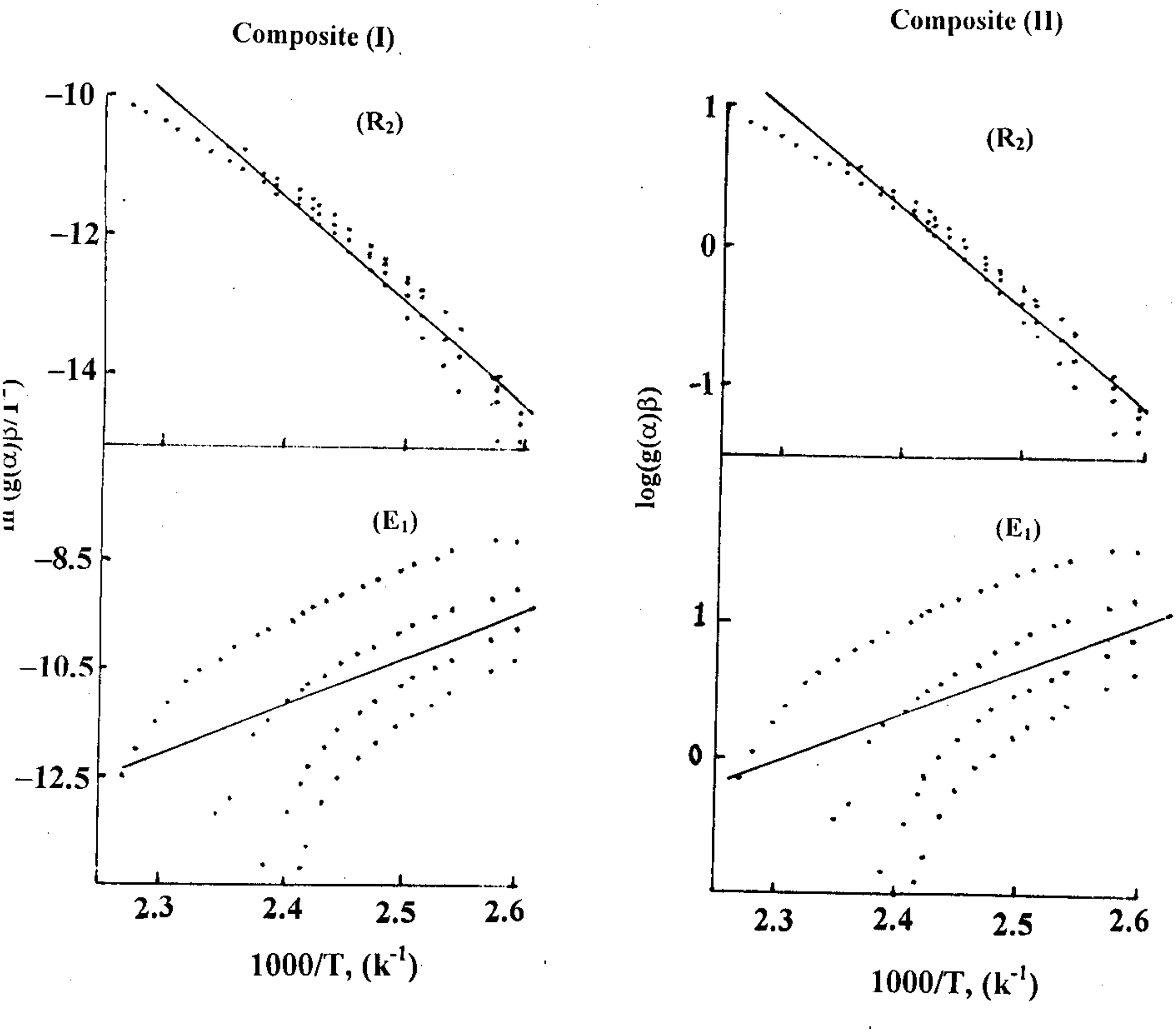

Fig.(III-A-9): Composite analysis of dynamic TG data of thermal dehydration of cobalt-nickel isonicotinate, assuming (R_2) and (E_1) models.

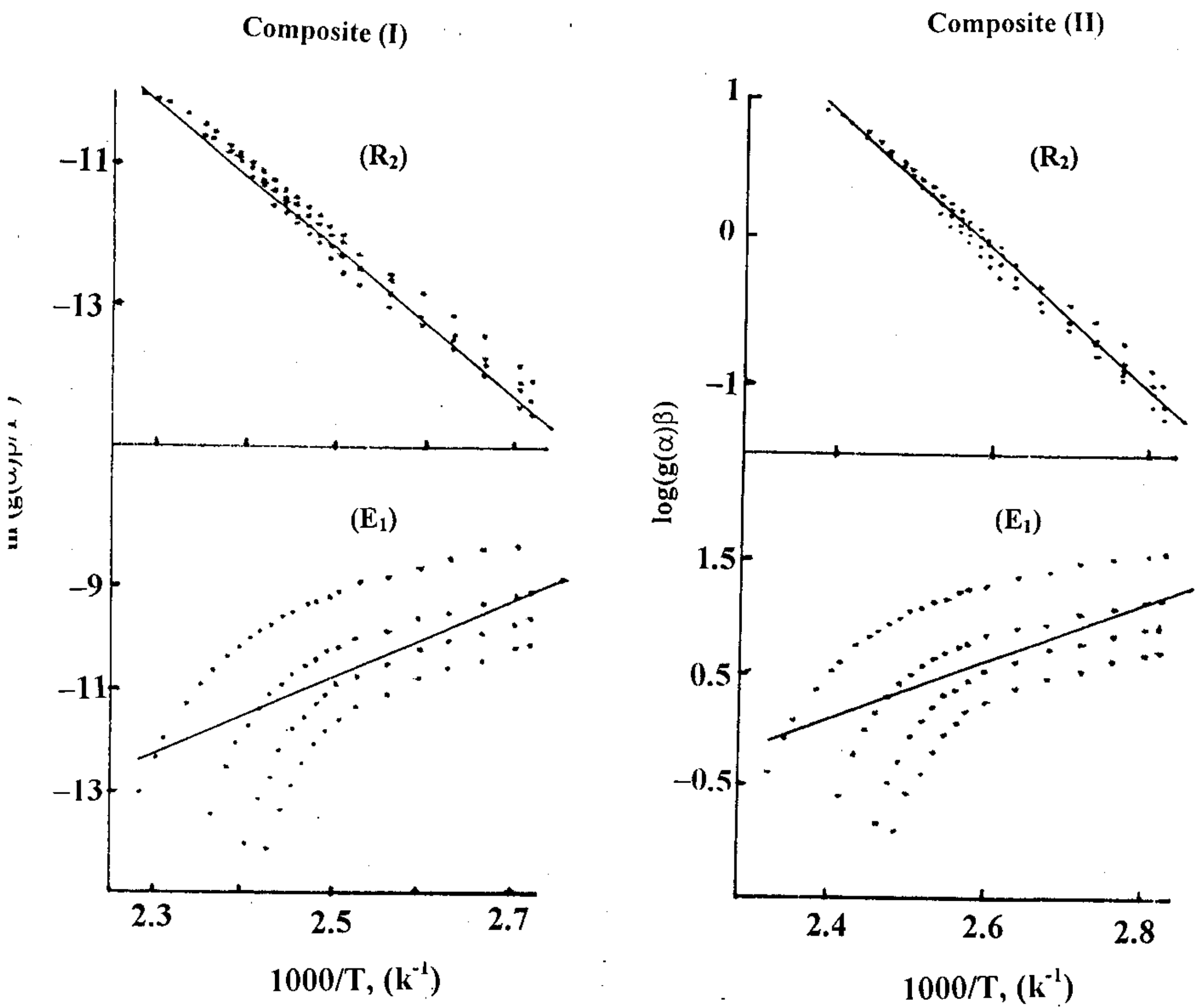

Fig.(III-A-10): Composite analysis of dynamic TG data of thermal dehydration of zinc nicotinate, assuming (R_2) and (E_1) models.

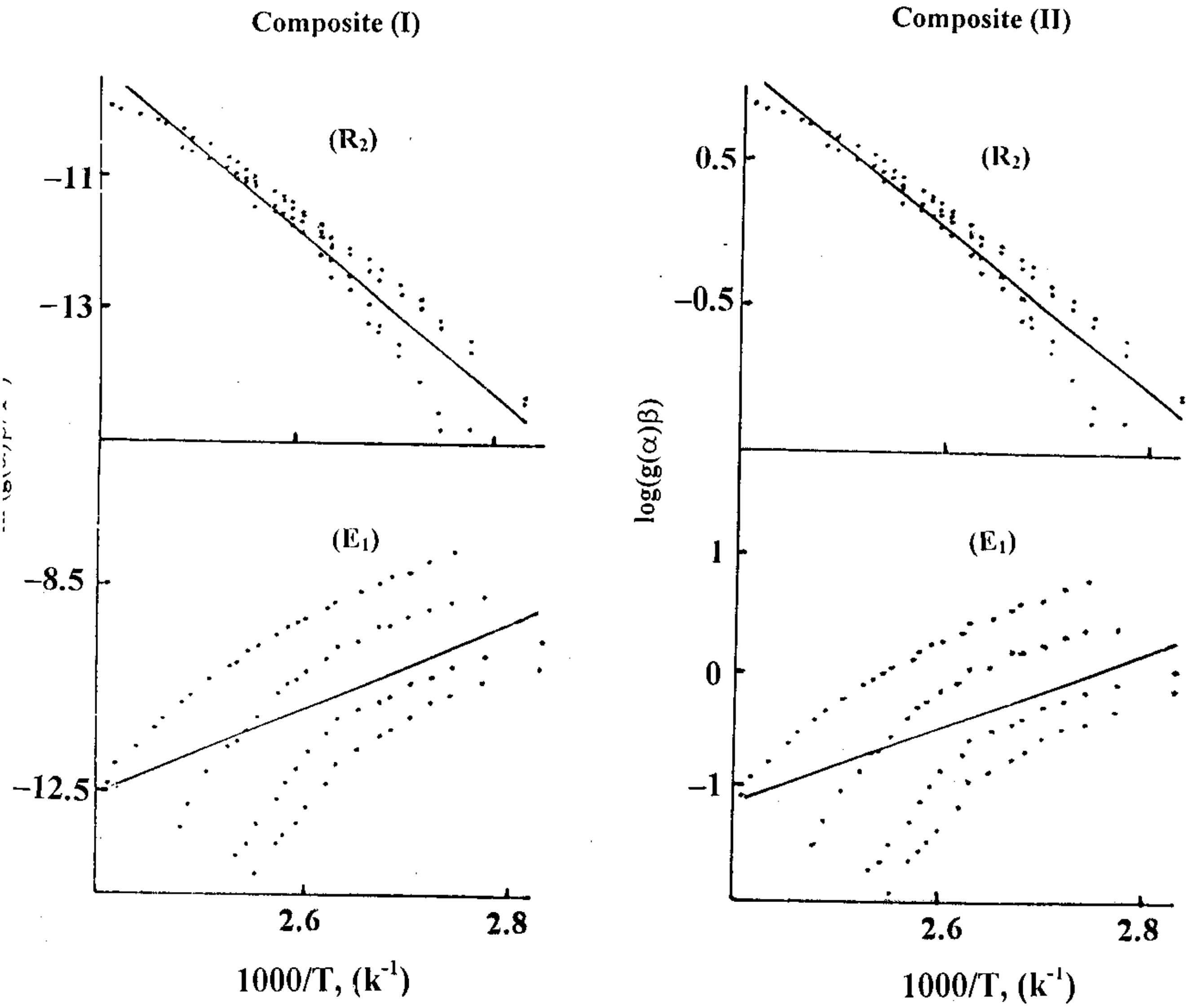

Fig.(III-A-11): Composite analysis of dynamic TG data of thermal dehydration of cupper isonicotinate, assuming (R_2) and (E_1) models.

It should be mentioned here that in spite of the great variation in each of the composition of the sample and their crystal structure, but all of them are dehydrated through phase boundary (R_2) model. It means that the cations do not play a role in the mechanism of dehydration, but it comes mainly from the moiety of ligand or water molecules. This may be explained on the basis of the large volume of ligand or great distribution of water molecules as compared with that of cations. The contact between that large moiety affects each others and causes the dehydration to proceed through R_2 mechanism.

An inspection of Table (III-A-3) shows that the activation energy of the dehydration process of nicotinic acid and its compounds decrease in the order calculated using composite methods:

Zinc-nicotinate > cobalt- nicotinate > nickel- nictoinate >
cobalt -nickle-nicotinate.

While for isonicotinic acid and its complexes decreases in the order:

cobalt-isonicotinate > nickel-isonicotinate > cobalt- nickel-isonicotinate >
copper isonicotinate.

The introducing of cations into the ligand molecule led to a change in the rate of dehydration, table (III-A-3). This is attributed to the change occurring in the chemical potential of the reactants and the transition states.

For determine the degree of disorder occurring during the thermal dehydration process $\Delta S^{\#}$ (the entropy of activation) was calculated using:

$$A = \frac{KT}{n} \exp \frac{\Delta S^{\#}}{R}$$

The results obtained are also given in table (III-A-3). The negative values of the entropy of activated obtained for the dehydration step indicates that the activated complex formed during the dehydration process are more ordered than the reactants, while the positive values of entropy obtained for the dehydration step indicate a higher ordering of the reactants than of the activated complex during the dehydration process.

Table (III-A-3): Kinetic parameters for investigated compounds calculated using different methods assuming R_2 model.

Compounds	Composite I		Composite II		Coats-Redfern		Ozawa		
	E, kJ mol^{-1}	Log A, min^{-1}	E, kJ mol^{-1}	Log A, min^{-1}	E, kJ mol^{-1}	Log A, min^{-1}	E, kJ mol^{-1}	Log A, min^{-1}	ΔS, Cal/mol. K
Cobalt nicotinate	115 ± 3.0	13.9 ± 0.8	116 ± 3	14 ± 0.4	126 ± 12	15.5 ± 1.7	96 ± 11	11.4 ± 1.4	4.37
Nickel nicotinate	113 ± 2.0	13.0 ± 0.60	114 ± 2	13.2 ± 0.3	120 ± 13	13.6 ± 1.7	117 ± 26	13.7 ± 3.6	0.37
Zinc nicotinate	135 ± 4.8	18.1 ± 1.60	134 ± 4.5	18 ± 0.7	140 ± 24	18.9 ± 3.4	109 ± 12	14.3 ± 1.8	23.97
Cobalt Nickel nicotinate	101 ± 2.0	11.8 ± 0.60	102 ± 1	12.1 ± 0.3	103 ± 11	12.3 ± 3.4	111 ± 22	13.3 ± 3.1	-5.02
Cobalt isonicotinate	125 ± 4.0	15 ± 1.30	124 ± 4	15.1 ± 0.6	136 ± 17	17.1 ± 2.4	94 ± 10	11.5 ± 1.3	9.58
Nickel isonicotinate	122 ± 4.0	14.1 ± 1.1	123 ± 4	14.2 ± 0.5	144 ± 15	18.2 ± 3.2	91 ± 9	10.2 ± 0.9	5.35
Copper isonicotinate	85 ± 1.0	10 ± 0.40	87 ± 1	10.4 ± 0.2	75 ± 4	8.7 ± 0.5	117 ± 13	15.1 ± 3.4	-13.46
Cobalt Nickel isonicotinate	122 ± 4.0	14.5 ± 1.1	122 ± 3	13.5 ± 0.5	132 ± 7	15.8 ± 0.9	94 ± 11	10.9 ± 1.3	7.33

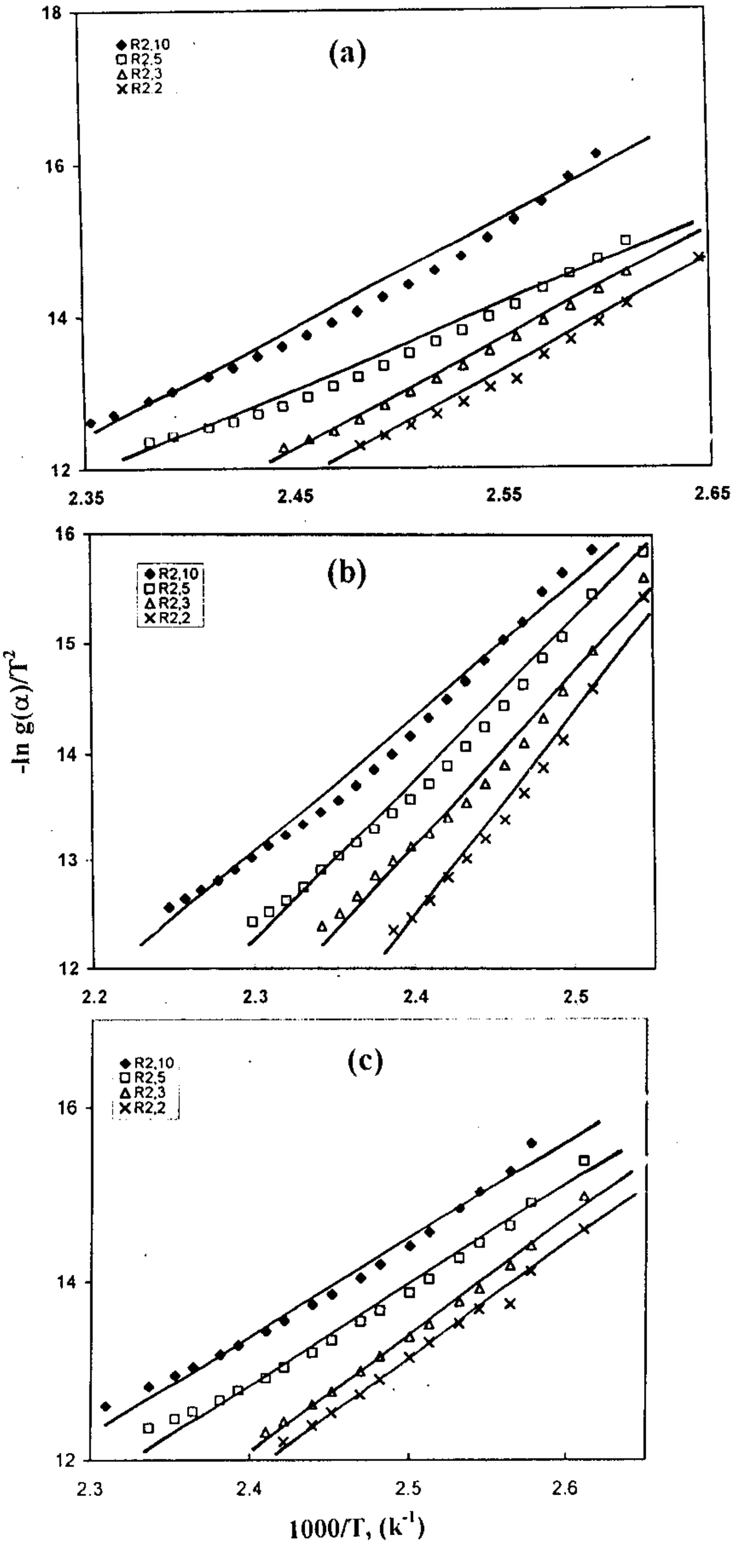

Fig.(III-A-12): Coats-Redfern method of analysis for dynamic dehydration of (a) cobalt nicotinate, (b) nickel nicotinate and (c) cobalt-nickel nicotinate, assuming (R_2) model.

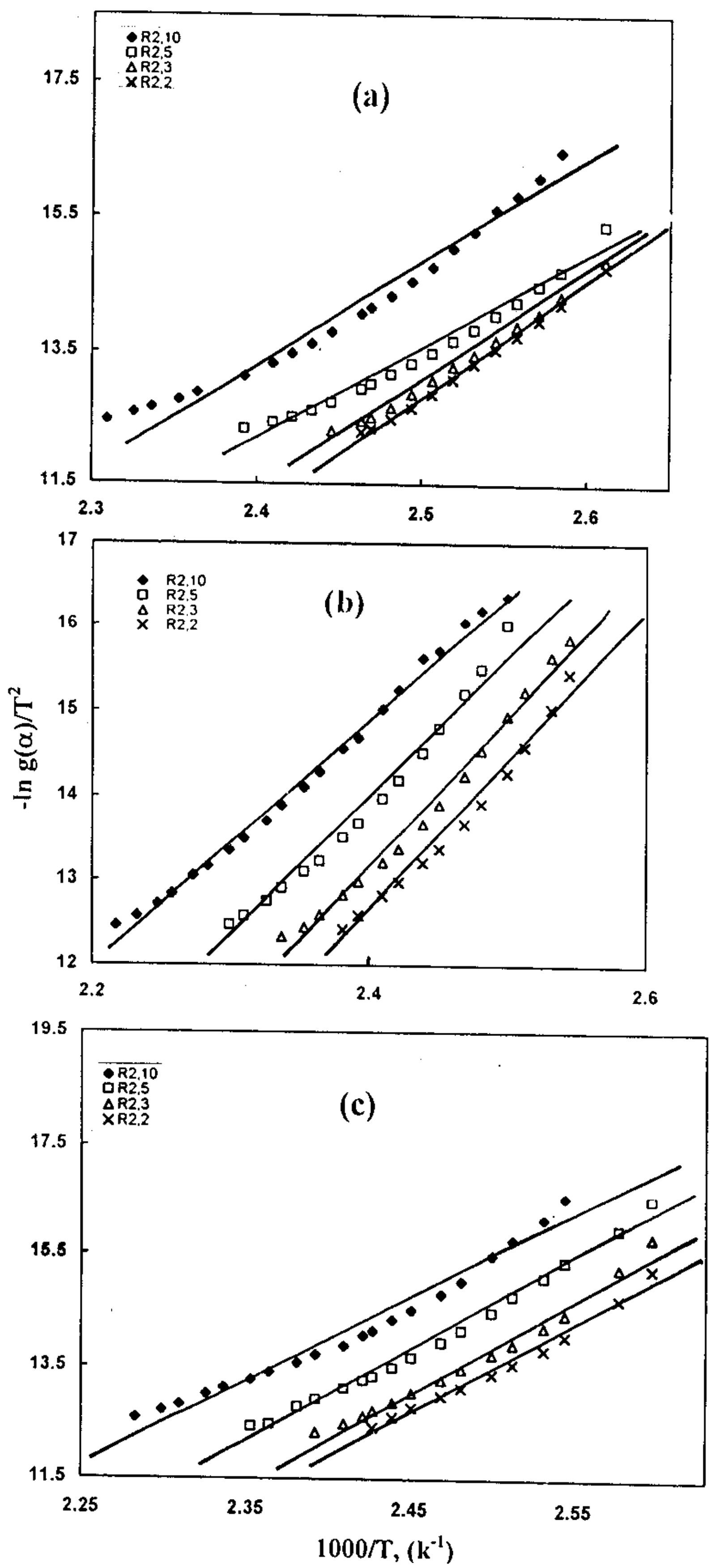

Fig.(III-A-13): Coats-Redfern method of analysis for dynamic dehydration of (a) cobalt isonicotinate, (b) nickel isonicotinate and (c) cobalt-nickel isonicotinate, assuming (R_2) model.

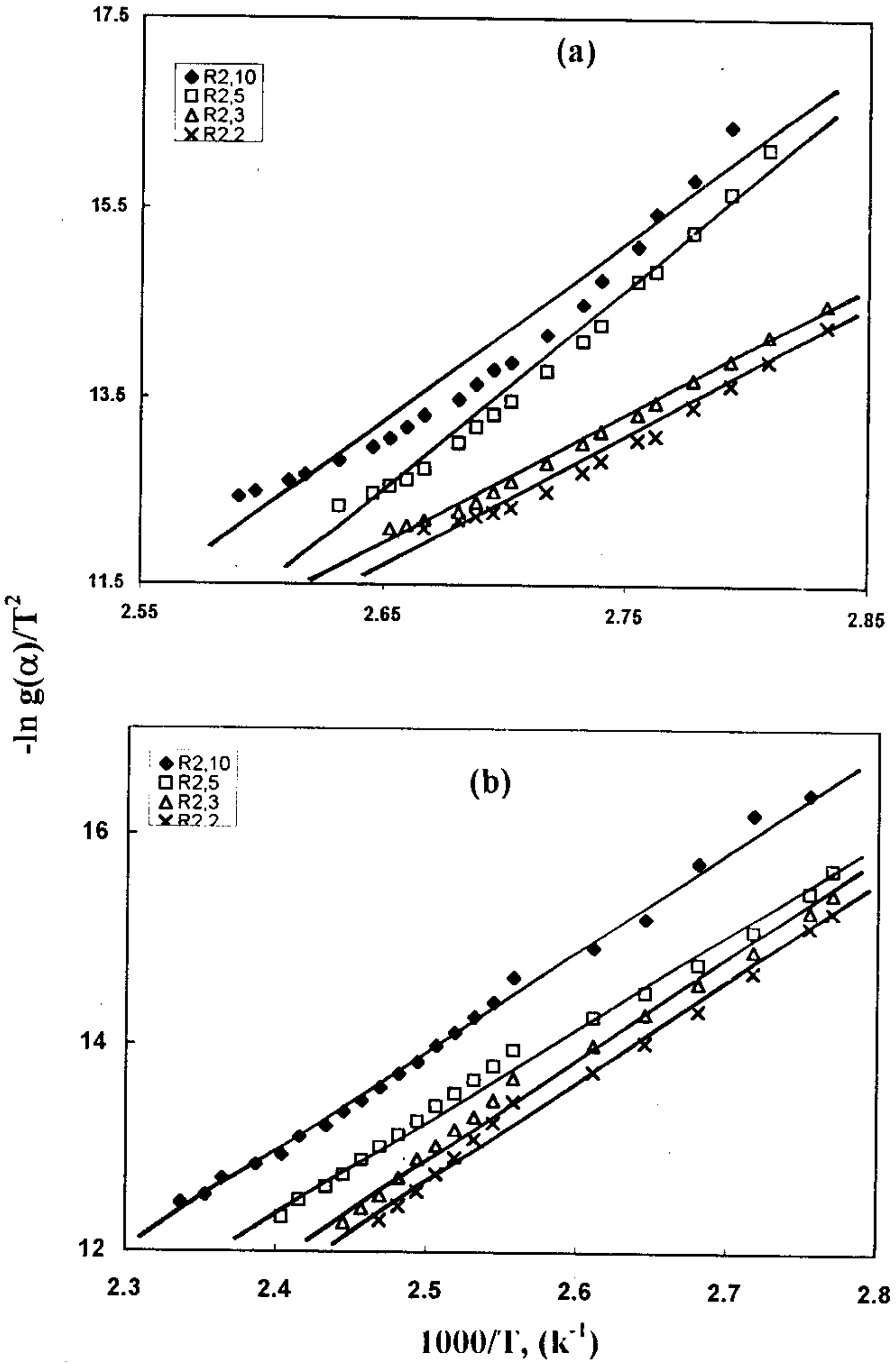

Fig.(III-A-14): Coats-Redfern method of analysis for dynamic dehydration of (a) zinc nicotinate and (b) cupper isonicotinate, assuming (R_2) model.

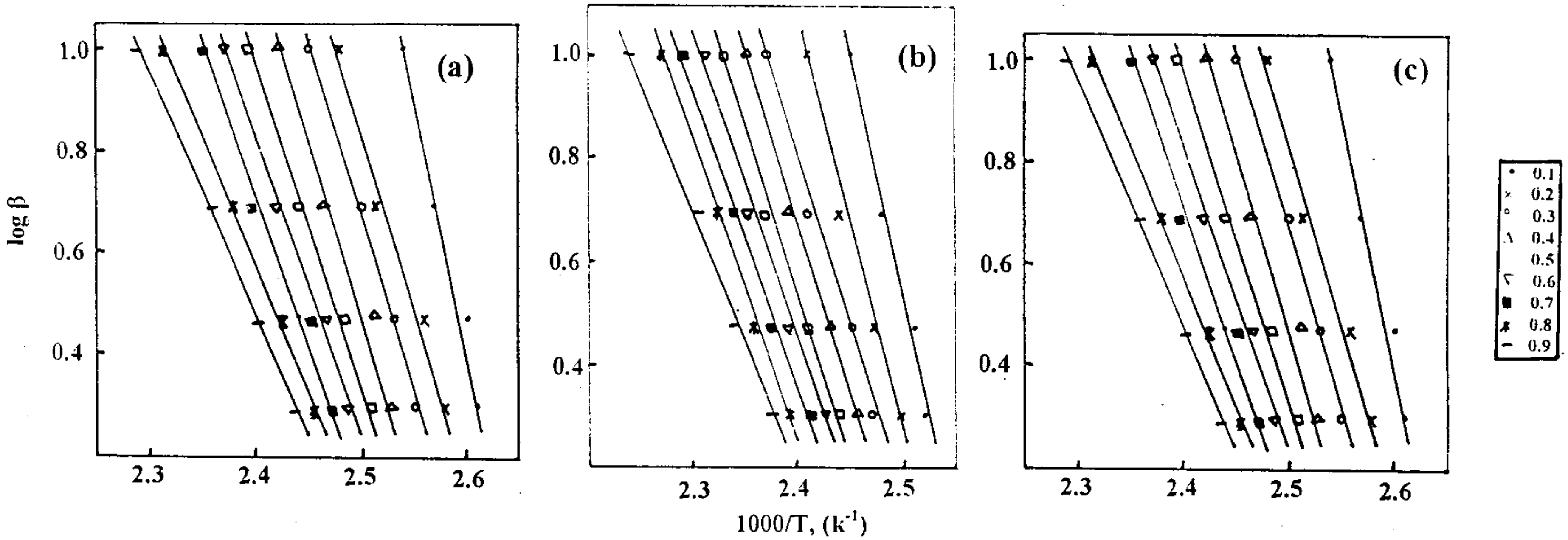

Fig.(III-A-15): Ozawa method of analysis for thermal dehydration of (a) cobalt nicotinate, (b) nickel nicotinate and (c) cobalt-nickel nicotinate.

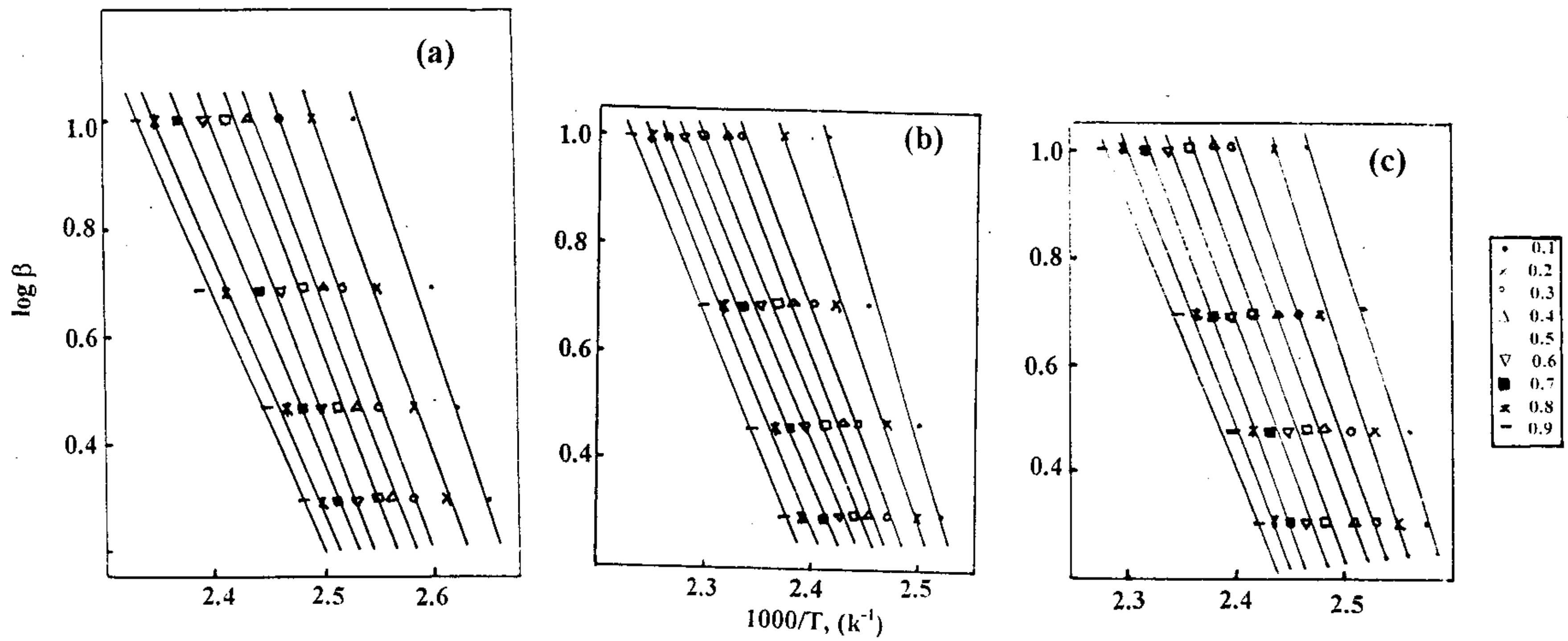

Fig.(III-A-16): **Ozawa method of analysis for thermal dehydration of** (a) **cobalt isonicotinate,** (b) **nickel isonicotinate and** (c) **cobalt-nickel isonicotinate**

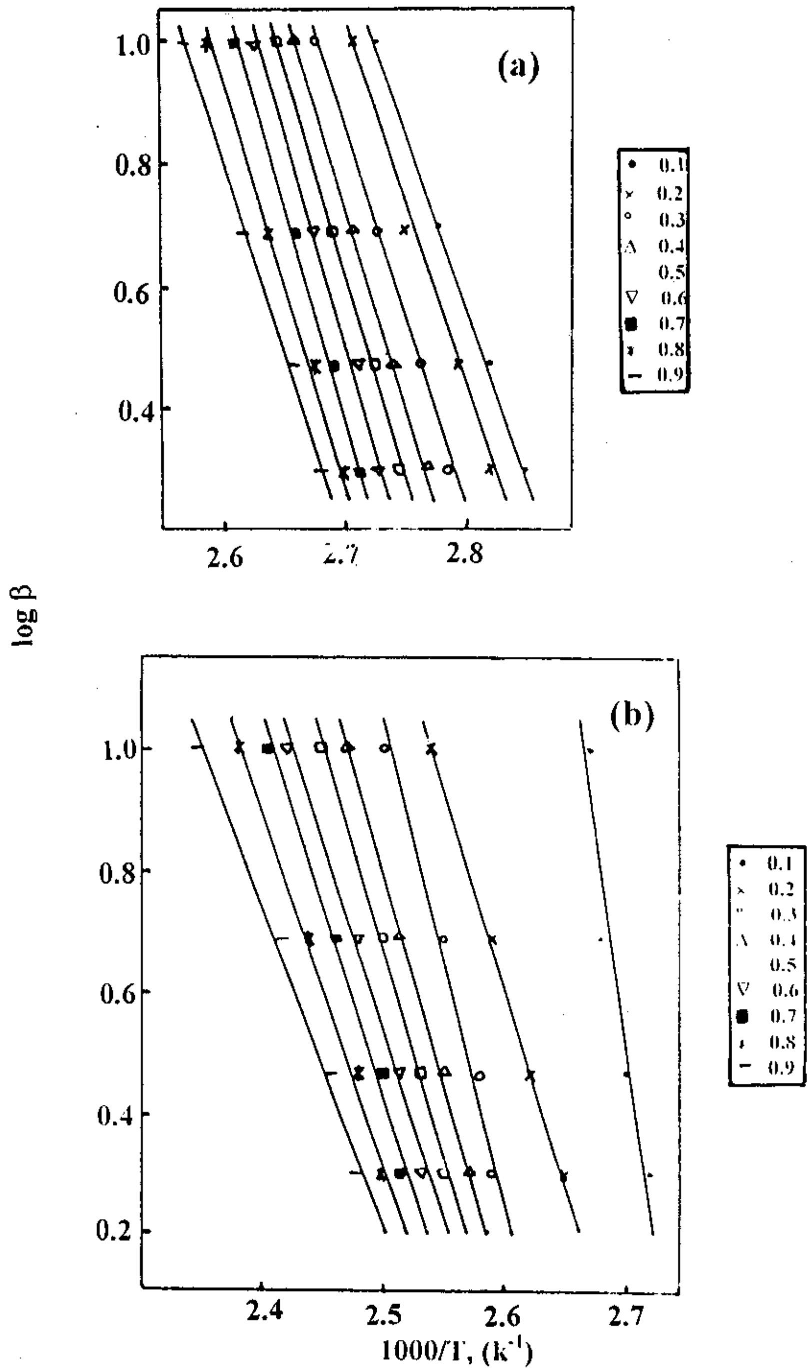

Fig.(III-A-17): Ozawa method of analysis for thermal dehydration of (a) zinc nicotinate and (b) cupper isonicotinate

Table(III-A-4): Kinetic parameters for investigated compounds calculated using different methods assuming R_3 model.

Compound	Composite I		Composite II		Coats-Redfern		Ozawa	
	E, kJ mol^{-1}.	Log A, min^{-1}	E, kJ mol^{-1}.	Log A, min^{-1}	E, kJ mol^{-1}.	Log A, min^{-1}	E, kJ mol^{-1}.	Log A, min^{-1}
Cobalt nicotinate	119 ± 3	14.3 ± 0.8	119 ± 3	14.4 ± 0.1	132 ± 11	16.2 ± 1.6	96 ± 11	11.3 ± 1.3
Nickel nicotinate	117 ± 2	13.5 ± 0.6	118 ± 2	13.6 ± 0.3	133 ± 26	15.5 ± 3.4	117 ± 26	13.5 ± 3.5
Zinc nicotinate	140 ± 4.9	18.7 ± 1.6	139 ± 4.6	18.6 ± 0.7	147 ± 23	19.8 ± 3.3	109 ± 12	10.7 ± 1.4
Cobalt Nickel nicotinate	150 ± 2	12.2 ± 0.6	106 ± 2	12.4 ± 0.2	108 ± 13	12.6 ± 1.8	111 ± 22	13.2 ± .3
Cobalt isonicotinate	128 ± 4	15.4 ± 1.3	128 ± 4	15.4 ± 0.6	145 ± 17	17.7 ± 2.1	94 ± 10	21.5 ± 3.4
Nickel isonicotinate	127 ± 4	14.5 ± 1.1	127 ± 4	14.6 ± 0.5	145 ± 14	17.4 ± 1.9	91 ± 9	10.1 ± 1
Copper isonicotinate	88 ± 1	10.3 ± 0.4	90 ± 1	10.6 ± 0.2	79 ± 14	8.8 ± 0.9	117 ± 13	16.1 ± 6.4
Cobalt Nickel isonicotinate	126 ± 4	14.8 ± 1.1	126 ± 3	14.9 ± 0.5	139 ± 8	16.6 ± 1.2	94 ± 11	10.7 ±1.5