

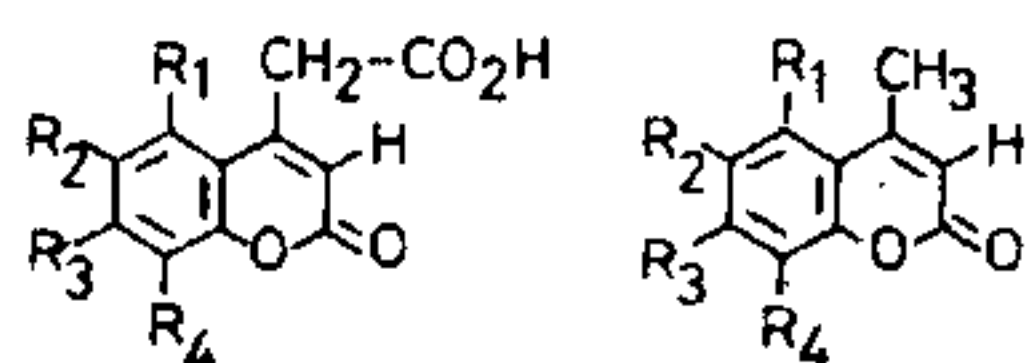
BASE-CATALYZED DECARBOXYLATION OF COUMARIN-4-ACETIC ACIDS

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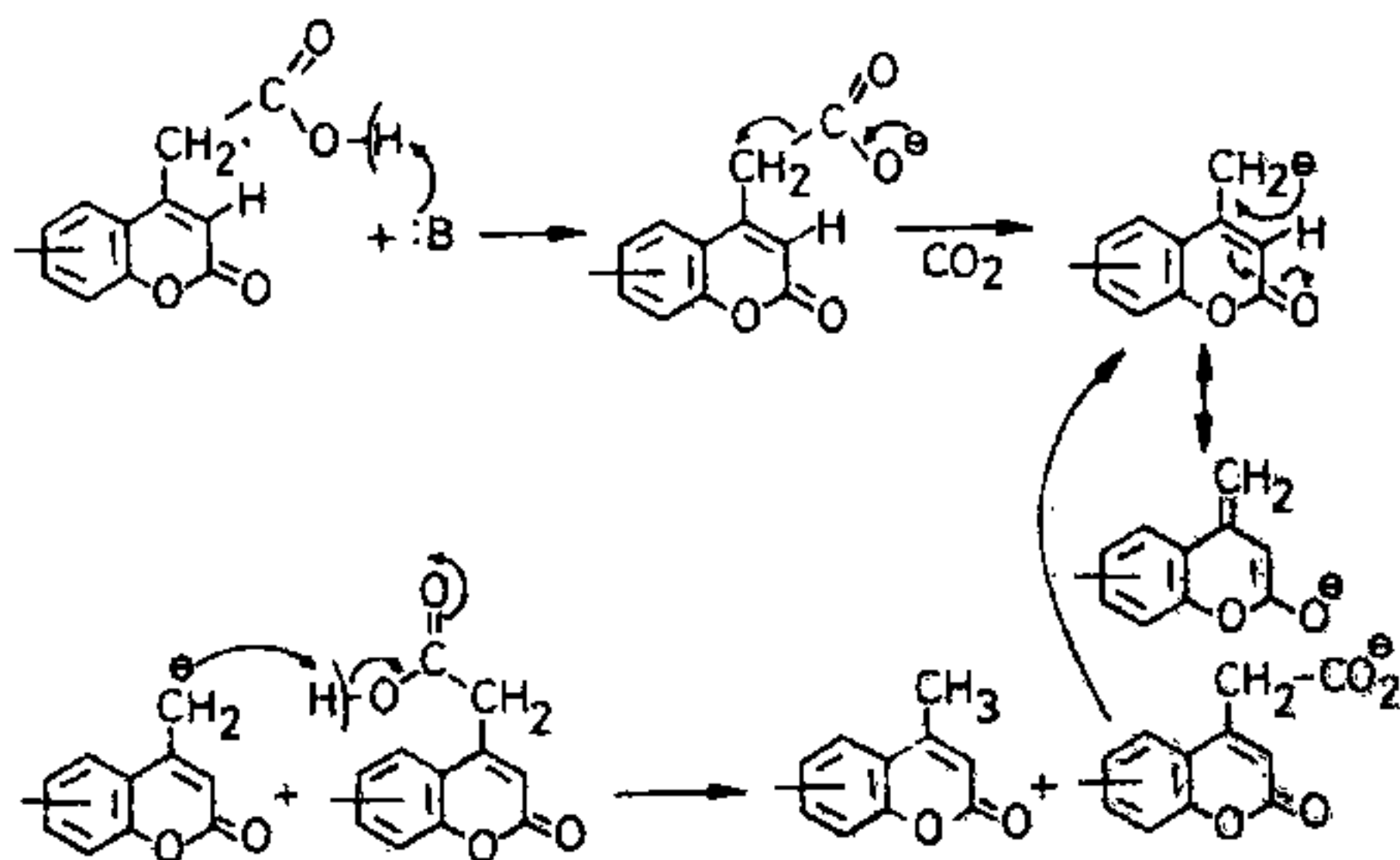
SUBSTITUTED coumarin-4-acetic acids¹ (1–5) attracted our attention in view of their optical (laser) properties², interesting mass spectral patterns resulting from decarboxylation and subsequent carbonylation², and their use as precursors for the synthesis of a number of heterocycles³. It was, however, observed that treatment of these acids (1, 3–5) with *o*-phenylenediamine in dimethylacetamide under refluxing conditions did not yield the expected imidazole but induced decarboxylation resulting in 4-methylcoumarins (6, 8–10). Even an attempt to convert these acids (1, 3–5) into anhydrides by treatment with potassium carbonate and ethylchloroformate in acetone at 0°C was not successful⁴ but only yielded 4-methylcoumarins (6, 8–10). On the basis of these observations, the acids (1–5) were treated with various reagents like β -phenethylamine (heating at 150°C), *N,N*-dimethylformamide, dimethylacetamide, dimethylsulphoxide (heating at 90°C) and it was observed that only 4-methylcoumarins (6–10) could be obtained⁵.

The evidence in favour of this intermolecular mechanism are:



- | | |
|---------------------------------|------|
| $R_1=R_2=R_4=H, R_3=CH_3$ (1) | (6) |
| $R_1=R_2=R_4=H, R_3=OH$ (2) | (7) |
| $R_1=R_2=R_4=H, R_3=OCH_3$ (3) | (8) |
| $R_1=R_2=H, R_3, R_4=benzo$ (4) | (9) |
| $R_3=R_4=H, R_1, R_2=benzo$ (5) | (10) |

To account for these observations, the following mechanism was proposed:



(a) Bromine or deuterium substituted 4-methylcoumarins were not obtained on treatment with bromine or deuterium oxide, after removal of solvent under reduced pressure. (b) It was observed that this reaction could be promoted even by catalytic amount of the base. (c) Deuterated acid (1) (i.e., deuterium substitution either at carboxyl group or at both carboxyl and active methylene group of substituted coumarin-4-acetic acid) also yielded mono and dideuterated 4-methylcoumarin (6). (d) 7-Hydroxycoumarin-4-acetic acid (2) yielded only the carboxylate salt on treatment with potassium carbonate and acetone, since the phenolate anion formed does not promote the decarboxylation. (e) The decarboxylation was not observed in aqueous or acidic conditions at room temperature. (f) Monitoring the concentrations of the acid or that of 4-methylcoumarins formed from the ¹H-NMR signal intensities of methylene protons or that of C₃-H, revealed that at low concentrations of the base, the decarboxylation reaction had a longer induction time.

Since the induction time showed an inverse relationship with base concentration, it is considered that the reaction between the anion formed and the free acid is the slow step, probably, due to diffusion limitations.

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5. Thermally induced intramolecular decarboxylation of coumarin-4-acetic acids were observed only when the acids were heated above their melting point¹. In the present investigation, thermal decarboxylation of the acids was not noticed when heated at 150°C at a pressure of 10⁻² torr. Hence the base catalyzed route alone was considered feasible.

POTENTIOMETRIC STUDIES ON MIXED-LIGAND BINUCLEAR COMPLEXES OF SOME TRANSITION METALS

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A review of the literature shows that mononuclear¹⁻³ mixed-ligand complexes of first row transition metals have been studied widely; however, scanty references are available on the study of formation of binuclear⁴⁻⁷ mixed-ligand complexes involving the above metal ions. The results of the studies on some binuclear mixed-ligand complexes of Cu(II), Ni(II), Zn(II) and Cd(II) formed by the simultaneous addition of the ligands EDTA and PDA to the metal ions have been reported in this communication.

Stock solutions of metal nitrates were prepared in double-distilled water and the metal contents of the solutions were estimated by standard methods⁸. The concentrations of all the solutions were checked potentiometrically. The pH-measurements were recorded with a Philips digital pH-meter having a working accuracy of ± 0.02 pH, using glass and calomel electrodes. The total volume (50 ml) and ionic strength ($\mu = 0.1, 0.2, 0.3$ M KNO₃) and the concentration of the metal and PDA (10×10^{-3} M), and EDTA (5×10^{-3} M) were kept constant at the beginning of each titration.

The dissociation constants of K₃EDTA ($pK_1 = 9.56$) and PDA ($pK_1' = 2.85$; $pK_2' = 5.09$)

were calculated by the method of Chaberck and Martell⁹ and the formation constants of the species 2 : 1 : 2 M (II) K₃EDTA-PDA using the expression of Gupta¹⁰.

Figure 1, curve b representing the titration of K₃EDTA exhibits no inflection indicating the non-labile nature of the remaining carboxy proton. Curve c depicting the titration of PDA exhibits inflection at $m = 1$ and $m = 2$ ($m =$ moles of base added per mole of metal ions or ligand) indicating the stepwise neutralization of the two carboxy protons of PDA.

Curve d representing the system 1 : 1 Cu(II)-K₃EDTA and curve e system 1 : 1 Cu(II)-PDA exhibit inflection at $m = 1$ and $m = 2$ which are attributed to the respective formation of 1 : 1 Cu(II)-K₃EDTA and Cu(II)-PDA binary species. An additional inflection at $m = 3$ in the case of 1 : 1 Cu(II)-PDA (curve e) may be attributed to the disproportionation of the initially formed 1 : 1 species, giving 1 : 2 Cu(II)-PDA species and metal hydroxide as may be clear by the following expression:

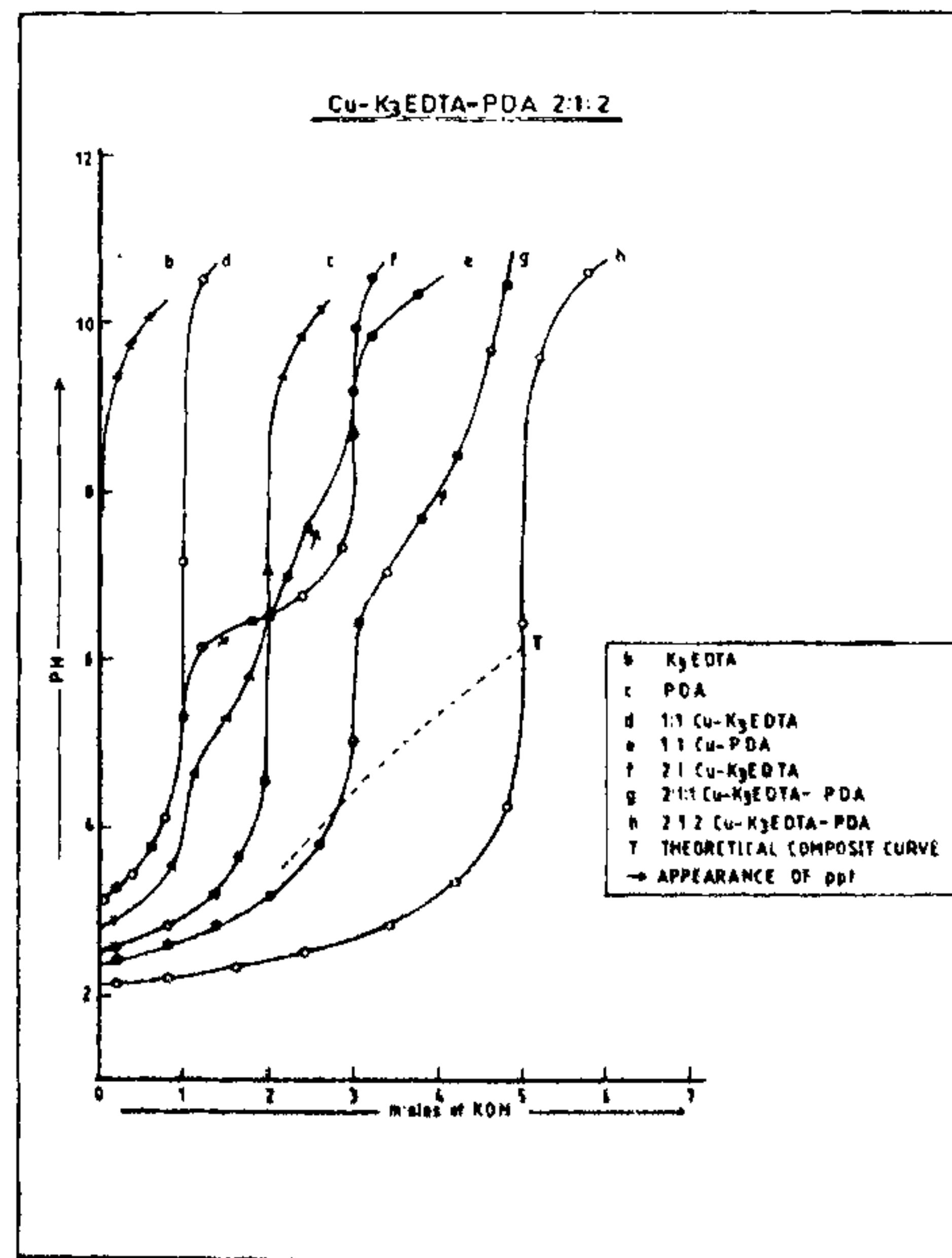


Figure 1. pH-titrations for the system: Cu(II)-EDTA-PDA; 2:1:2.