LINEAR FREE ENERGY RELATIONS
IN SOLID STATE REACTIONS II

Phase boundary processes in reactions of cobalt acetate
with aniline hydrochlorides

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Kinetics of the reaction between solid cobalt(II) acetate and solid substituted aniline hydrochlorides have been studied by thermal analysis. All the reactions go to completion. The crystalline products were characterized by physico-chemical methods. The energy of activation is 83.4, 44.2, 64.2, 100.9, 79.8, 99.9, 135.9 and 168.7 kJ mol^{-1} for the reactions of aniline, 3- and 4-chloro-, 4-iodo-, 4-bromo-, 4-fluoro-, 4-methyl- and 4-methoxy aniline hydrochlorides with cobalt acetate. A plot of energy of activation against Hammett's σ constant is linear with a slope of -169.9 kJ mol^{-1}. A comparison between the reactivity of these reactions by the capillary and the thermal methods has been done.

Application of Hammett equation to a solid phase reaction series between cobalt acetate and aniline hydrochlorides has been reported earlier using the capillary technique in which the rate is measured by noting the increase in thickness of the product boundary formed at the junction of reactants in a capillary, in which the diffusing species is the aniline salt [1, 2]. Apart from it's limited application to coloured products, a large number of reaction parameters, such as a well defined particle size, constant compaction and also specific diameter of the capillary is needed for absolute rates. Because of these limitations and even after overcoming them, the rates may always be relative [3]. The particles being immobile in the capillary, the reaction becomes diffusion controlled soon after the initial product boundary is formed. The diffusion is also of two types (i) surface migration over the particles or vapour phase diffusion and (ii) the bulk diffusion within the grains. Therefore it would be very desirable to use a technique with which one could obtain kinetic data for at least the true chemical reaction steps or the phase boundary processes of the overall solid state reaction to be able to tell whether the Hammett equation or other rules of physical organic chemistry [4], derived almost exclusively from studies of

solution processes are applicable also to solids. The Hammett equation should apply to reactions which satisfy the following conditions:

1. All reactants of a series are isostructural, and either all the reactants of the series have a polar axis [5] or none has one.

2. The products should be isostructural.

3. The nature of binding i.e. ionic or covalent, should be the same throughout the series and

4. throughout the reaction series, the rate constants obtained from the same kinetic model should be used. It has been noted that kinetic parameters depend largely on the reaction model and that similar compounds react according to different reaction models.

On the basis of information available in literature [6–12] and the investigations described here, it can be safely concluded that the above stated conditions are met for most of the reactants (except aniline hydrochloride) reported here. It is claimed that the rates obtained by mass loss method and especially the rates determined for initial reaction represent the true phase boundary processes as against the rates obtained in capillary technique where the rates are a measure of the sum of the diffusion and phase boundary processes.

Experimental

Materials

Cobalt acetate (AR) was dehydrated at 413 K for six hours. The composition of anhydrous sample was determined volumetrically for cobalt, % found 33.0 (calcd. 33.3). Aniline salts were prepared by passing dry hydrogen chloride gas through an ethanolic solution of the respective amines. The hydrochlorides were purified by recrystallization and their purity was checked by determining the chlorine content (Table 1). The compounds were sieved to a fixed mesh size, using B.S.S. standard sieves. Corresponding products from the solution phase were prepared by known methods.

The reflectance spectra and infrared spectra were recorded on a Carl-Zeiss VSU–2P type spectrophotometer and SP3–300 Pye-Unicem instrument in MgO and KBr respectively. Magnetic moment studies were done on a Gouy balance. DTA–TG–DTG studies were done on a Stanton–Redcroft STA–780 thermal analyzer in nitrogen atmosphere (50 ml per min) at a heating rate of 5 deg/min. The amount of sample used was 15–20 mg.

Table 1 Microanalysis results[a] of the solid phase products $CoCl_2 \cdot 2(XC_6H_4NH_2)$

X	C	H	N	Co	Cl
3-Cl	37.99 (37.40)	4.81 (3.17)	7.01 (7.27)	15.73 (15.32)	17.44 (18.44)
4-Cl	35.87 (37.40)	3.88 (3.17)	6.30 (7.27)	15.71 (15.32)	18.82 (18.44)
4-I	24.80 (25.35)	2.64 (2.11)	4.12 (4.93)	10.61 (10.38)	11.96 (12.50)
4-Br	30.92 (30.38)	2.42 (2.53)	6.25 (5.91)	12.39 (12.45)	14.62 (14.98)
4-F	40.23 (40.91)	3.08 (3.41)	8.09 (7.95)	16.81 (16.76)	19.76 (20.17)
H	44.86 (45.57)	4.49 (4.43)	8.14 (8.86)	18.11 (18.67)	21.60 (22.47)
4-CH$_3$	47.93 (48.84)	5.92 (5.23)	8.42 (8.14)	17.52 (17.15)	20.41 (20.64)
4-OCH$_3$	43.59 (44.65)	4.32 (4.78)	6.97 (7.44)	15.50 (15.68)	18.92 (18.87)

[a] Some of these results have already been reported (1). The values in parenthesis are the calculated ones.

Kinetics

The kinetics of these reactions was studied by TG. Acetic acid is the only gaseous reaction product and therefore loss in weight of the mixture is a direct measure of the extent of reaction. 0.001 moles of cobalt acetate were weighed and intimately mixed with 0.002 moles of the aniline salt. The particle size of all the reactants used for these studies is 44 ± 2 μ. Mixing was done with special care so as to get best possible homogeneity under minimum of pressure. The mixture was taken in a thin glass bucket, which was suspended in a thermostat (± 0.1 K) and connected to the pan of an electrical balance (0.01 mg) with a platinum wire. Change in weight was recorded with time.

Results and discussion

Reactions of solid anhydrous cobalt acetate with substituted solid aniline hydrochlorides (3-Cl, 4-Cl, 4-I, 4-Br, 4-F, 4-CH$_3$, 4-OCH$_3$ and H) give bis aniline cobalt(II) chloride complexes and a gaseous product. The gases evolved were tested for the presence of chloride with silver nitrate, for water with anhydrous copper sulphate and with lime water for carbondioxide. The tests showed the absence of hydrogen chloride, carbondioxide and water in the gaseous product. It was identified to be only acetic acid from it's smell and other tests.

The products from the solid phase reactions were prepared by mixing fine powder in 1 : 2 stoichiometric ratio of the reactants. They were intimately mixed in a pestle mortar and kept in a thermostat at 393 K for 24 hr. No eutectic formation or melting was detected. In each case loss in weight corresponding to 2 mole of acetic

Table 2 Thermal analysis results for the fresh mixture (1 : 2) of cobalt acetate with substituted aniline salts

	Weight, %	Temp. range, K
1 3-chloroaniline hydrochloride	23.0 (23.7)*	364–393
2 4-fluoroaniline hydrochloride	25.4 (27.0)	375–423
3 Aniline hydrochloride	26.5 (27.5)	380–406
4 4-toluidene hydrochloride	28.0 (28.0)	400–433
5 4-anisidine hydrochloride	23.0 (24.1)	408–420

* Values in braces are the calculated ones for the expected loss of 2 moles of acetic acid.

acid was observed. The solid phase products were analyzed for Co, Cl, C, H and N content and the results are given in Table 1. The data is consistent with the formulation $CoCl_2 \cdot 2(XC_6H_4NH_2)$.

Thermoanalytical curves for the fresh mixtures of the reactants were recorded to get an insight into the thermal changes in these reactions. Cobalt acetate does not show any melting or decomposition change below 473 K. All the amine salts melt or decompose above 473 K. TG of the fresh mixtures of cobalt acetate and aniline salts (1 : 2) shows a weight loss in the temperature range 365–430 K. This step corresponds to the reaction between cobalt acetate and aniline hydrochlorides as there is no change in the reactants at this temperature. The loss in weight corresponds to the elimination of two mole of acetic acid (Table 2) according to the stoichiometric equation. The solid-solid chemical reaction is endothermic and no

Table 3 Infrared, reflectance, magnetic moment and TLC results of the solid phase products

Product	IR, cm^{-1}					μ_{eff}, B.M.	λ_{max}, mm	TLC Rf
	v_{asym}, NH$_2$	v_{sym}, NH$_2$	v_{N-H-X}	v_{Co-N}	v_{Co-Cl}			
$CoCl_2 \cdot 2(3\text{-}ClC_6H_4NH_2)$	3260	3210	3120	432, 395	322, 302	4.53	637	0.89
$CoCl_2 \cdot 2(4\text{-}ClC_6H_4NH_2)$	3300	3255	3160	428, 385	320, 302	4.50	635	0.82
$CoCl_2 \cdot 2(4\text{-}IC_6H_4NH_2)$	3260	3220	3120	430, 390	325, 300	4.70	635	0.72
$CoCl_2 \cdot 2(4\text{-}BrC_6H_4NH_2)$	3290	3240	3145	420, 380	300	4.60	632	0.79
$CoCl_2 \cdot 2(4\text{-}FC_6H_4NH_2)$	3280	3235	3190	425,390	315	4.72	634	0.49
$CoCl_2 \cdot 2(C_6H_5NH_2)$	3265	3220	3125	410	320	4.50	637	0.69
$CoCl_2 \cdot 2(4\text{-}CH_3C_6H_4NH_2)$	3280	3235	3140	427	310	4.60	632	0.81
$CoCl_2 \cdot 2(4\text{-}OCH_3C_6H_4NH_2)$	3270	3225	3130	432	320	4.65	635	0.63

characteristic effect corresponding to the reactants is observed, which shows that reactants are completely consumed in the reaction step and that the reaction goes to completion. No melting was observed during the reaction. The product formed then decomposes with a loss in TG corresponding to the elimination of gaseous amines. The TG/DTA of the fresh mixture of cobalt acetate and 4-toluidine hydrochloride is shown in Fig. 1.
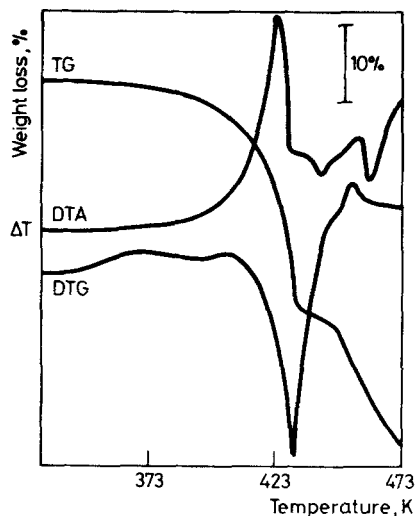

Fig. 1 TG–DTA of $Co(CH_3COO)_2$ and $C_6H_3NH_3Cl$ fresh mixture in $1:2$ stoichiometric ratio

In the infrared spectra, free primary amines exhibit N—H stretchingvibrations as doublet of medium intensity at 3400 and 3500 cm^{-1}, N—H bonding vibrations at 1650–1590 cm^{-1} and C—N vibrations at 1340–1250 cm^{-1}. Amine salts, N^+—H, show absorption owing to N—H stretching vibrations in the region ~ 3080 cm^{-1} and absorption owing to N—H bending vibrations at 1658–1608 cm^{-1} and 1550–1484 cm^{-1}. In addition they exhibit multiple combination bands and overtones at 2500 and 2000 cm^{-1}. The infrared spectra of the solid products show a doublet at 3300–3200 cm^{-1} due to asymmetric and symmetric N—H stretch. The lowering of N—H by 150–200 cm^{-1} from the free amine is indicative of the coordination of nitrogen to cobalt. Co—Cl and Co—N stretching vibrations are present at 430–380 and 330–280 cm^{-1} (Table 4). There are no bands due to NH_3^+ or free —NH_2 groups. Infrared spectra for the system cobalt acetate + aniline hydrochloride are shown in Fig. 2. Aniline hydrochloride has bands at 1970 and 2750 cm^{-1} (I). The spectrum of the solid phase reaction product (III) has bands at 3220 and 3265 cm^{-1} and that of the solution phase reaction product (IV) at 3250 and 3270 cm^{-1}. The spectrum of freshly mixed reactants (II)

Table 4 X-ray diffraction data for some of the products of solid state reactions between cobalt acetate and aniline hydrochlorides

4-ClC$_6$H$_4$NH$_3$Cl	4-FC$_6$H$_4$NH$_3$Cl	C$_6$H$_5$NH$_3$Cl	4-CH$_3$C$_6$H$_4$NH$_3$Cl	4-OCH$_3$C$_6$H$_4$NH$_3$Cl
11.282 m	14.470 vw	7.911 w	11.613 m	7.681 s
8.439 w	10.010 vw	7.351 w	10.033 vw	6.986 s
7.464 w	8.439 s	6.445 w	8.439 w	5.286 m
6.623 w	6.651 m	5.735 m	7.363 vw	4.997 vw
6.306 vw	5.691 m	5.273 m	5.990 w	4.508 w
5.986 vw			5.575 w	4.299 w

w = weak; vw = very weak
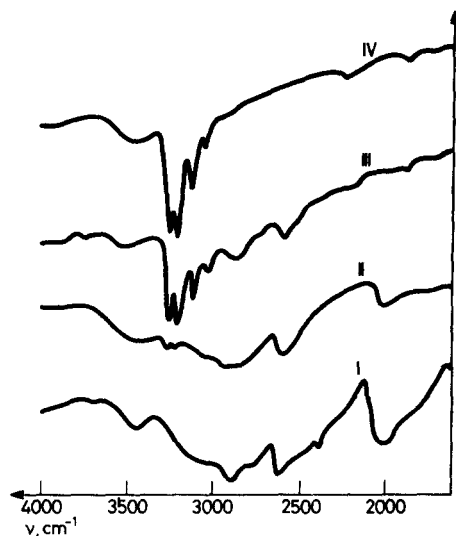
Fig. 2 Infrared spectra for the system cobalt acetate aniline hydrochloride. I – aniline hydrochloride, II – freshly mixed reactants, III – Solid phase product, IV – solution phase product

shows weak bands due to coordinated —NH_2 group i.e. there is some reaction immediately on mixing.

The reflectance spectra of the solid products show only one absorption band due to $4A_2 \rightarrow {}^4T_1(P)$ transition at 15000 cm^{-1} which is characteristic for tetrahedral cobalt(II) complexes. The values for the magnetic moment of the complexes (4.4–4.7 B.M.) are also in accordance with tetrahedral stereochemistry. Comparison of X-ray powder diffraction data (Table 4) of the products obtained from solid

Table 5 Values of energy of activation by the capillary technique and mass-loss method

X	E, kJ mol^{-1}	
	capillary	mass-loss
3-Cl	—	44.2
4-Cl	104.6	64.2
4-I	—	100.9
4-Br	102.9	79.8
4-F	120.4	99.9
H	—	83.4
4-CH$_3$	148.6	135.9
4-OCH$_3$	162.3	168.7

and solution phase reactions shows that the products are crystalline and that the products obtained in both cases are same. The solid phase reactions go to completion as evidenced by the absence of lines characteristic of reactants, in the spectra of products. The TLC of the products show single spot and R_f values for the solid and solution phase products are identical. Thus the spectral, elemental and thermoanalytical data show that the products are tetrahedral with the formula $CoCl_2 \cdot 2(XC_6H_4NH_2)$.

For analysing kinetic data it is essential to appreciate the difference between capillary technique and mass loss method for the same reaction. Because of the differences in lattice structures and lattice parameters of products and reactants, the product/reactant interface is not coherent. Soon the product peels off from the reactant to give fresh reactant surface for reaction. In the capillary technique, peeling off of the product may/do occur, yet in view of the build up of the product layer between the two reactants, tne reactants have to diffuse or migrate over the product layer for the reaction to progress. In the mass loss method the two reactants are intimately mixed, so that the product peels away soon after forming (it does not pile up between reactants, but separates as shaken) and the reaction remains phase boundary controlled with minimum of diffusion.

The kinetic results for the reactions of cobalt acetate with aniline hydrochlorides in $1:2$ ratio by the mass loss method are given in Figs 3–10, in which α, the
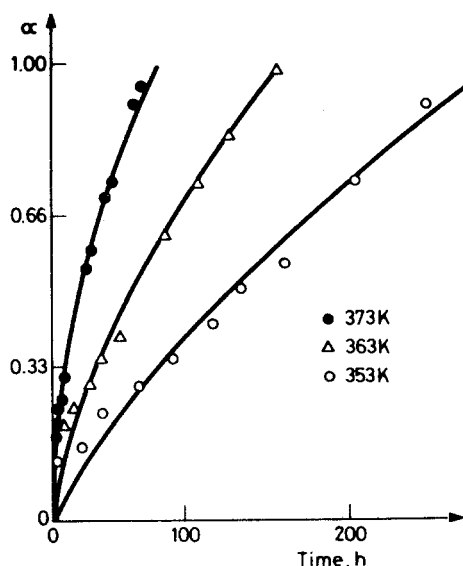

Fig. 3 Kinetic data for the reaction between $Co(CH_3COO)_2$ and $3\text{-}ClC_6H_4NH_3Cl$ by mass-loss method.
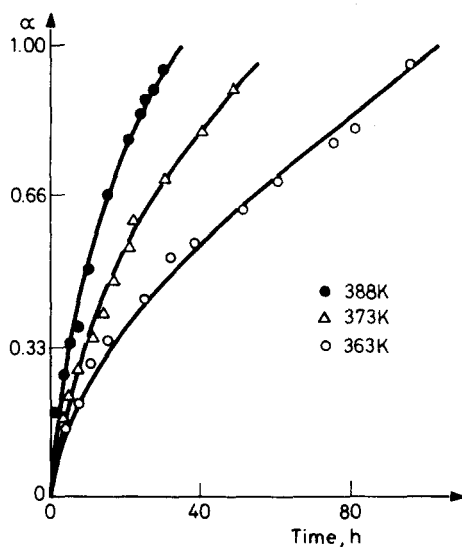
Fig. 4 Kinetic data for the reaction between $Co(CH_3COO)_2$ and $4\text{-}IC_6H_4NH_3Cl$ by mass-loss method.
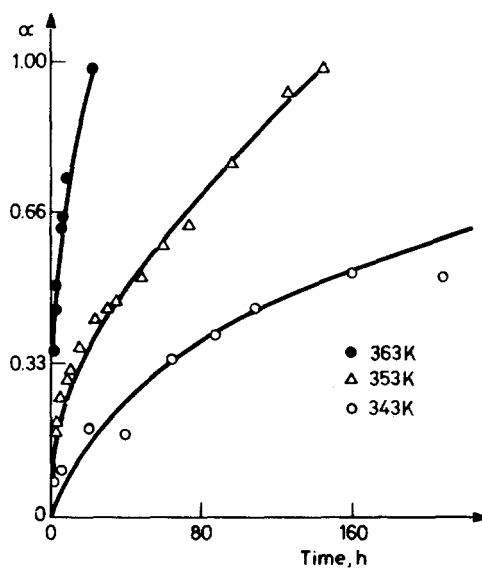
Fig. 5 Kinetic data for the reaction between $Co(CH_3COO)_2$ and $4\text{-}ClC_6H_4NH_3Cl$ by mass-loss method.
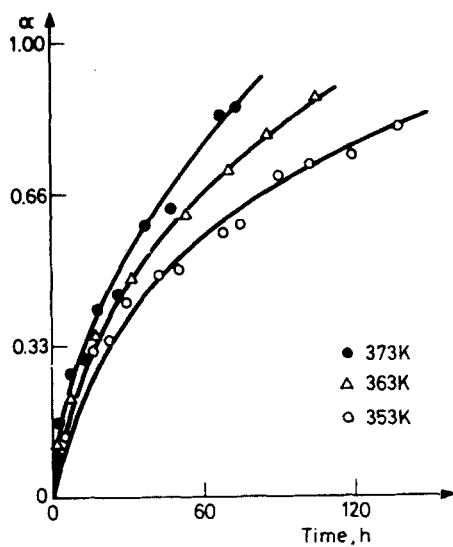
Fig. 6 Kinetic data for the reaction between $Co(CH_3COO)_2$ and $4\text{-BrC}_6H_4NH_3Cl$ by mass-loss method.
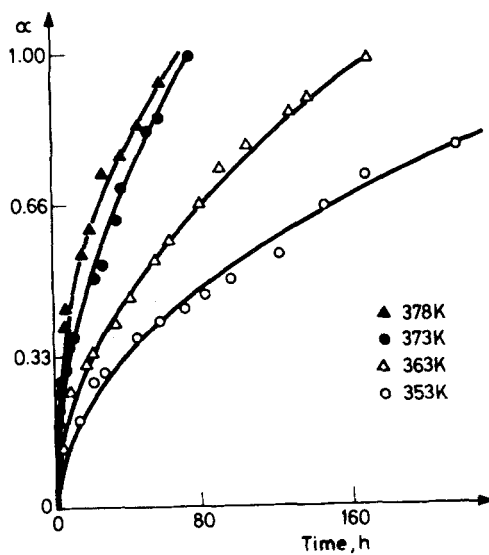
Fig. 7 Kinetic data for the reaction between $Co(CH_3COO)_2$ and $4\text{-FC}_6H_4NH_3Cl$ by mass-loss method.
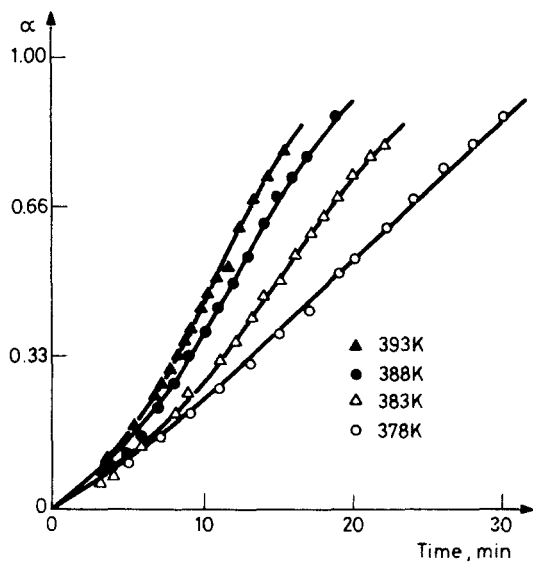
Fig. 8 Kinetic data for the reaction between $Co(CH_3COO)_2$ and $C_6H_5NH_3Cl$ by mass-loss method.
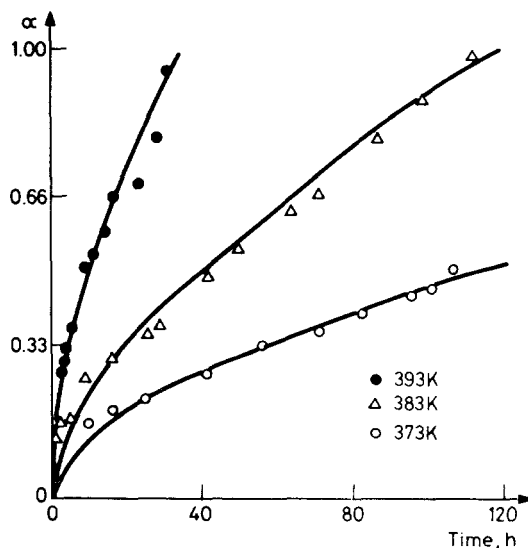
Fig. 9 Kinetic data for the reaction between $Co(CH_3COO)_2$ and $4\text{-}CH_3C_6H_4NH_3Cl$ by mass-loss method.
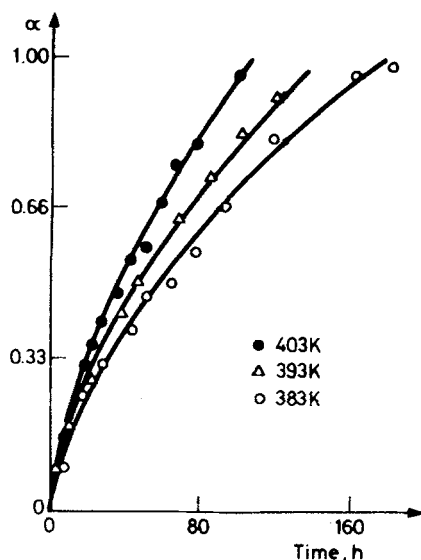
Fig. 10 Kinetic data for the reaction between $Co(CH_3COO)_2$ and $4\text{-}OCH_3C_6H_4NH_3Cl$ by mass-loss method.

fractional reaction is plotted against time. Figs 4–7, 9 and 10, for X = 4-I, 4-Cl, 4-Br, 4-F, 4-CH$_3$ and 4-OCH$_3$ show that the reaction is deceleratory throughout and in Figs 3 and 8 for X = H and 3-Cl, the reaction is initially acceleratory followed by large linear region with a decay at the end. Non-obedience of the linear plot for all the reactions throughout the entire range shows that phase boundary processes alone are not significant, and in this technique also diffusion plays a role.

The analyses of the isothermal kinetic data is usually made from the best fit of the α-time values for a number of rate equations derived for different geometric models. If several kinetic equations give good correlation with measured rate data, then it is difficult to assign mechanism on the basis of this data alone. For the calculation of activation energy, the choice of appropriate kinetic model is essential. Galwey [13] has argued that the magnitude of E can be accepted as a valuable method for comparing the reactivity of solids and that the values of E are comparatively insensitive to the particular rate equation used for the kinetic analysis, always provided that the power law is based on $(kt)^n$ and not kt^n. As such, the kinetic results were analyzed by the general equation $\alpha^n = kt$, where α is the fractional reaction and k and n are constants. The values of energy of activation as calculated from the Arrhenius equation are given in Table 5.

Plot of Hammett's σ constant, which is a measure of the combined resonance and inductive capability of the substituent to transmit the substituent electronic effect,

against energy of activation is linear for most of the substituents studied (Fig. 11). Usually Hammett's relation is tested for σ against log k, but as E is a function of log k so one can test the validity of Hammett's equation by plotting σ against E as well. The overall correlation coefficient is 0.93 with a slope of -170 KJ mol^{-1}. However, a good linear plot with a correlation coefficient of 0.99 and a slope of -183 KJ mol^{-1} is obtained if the values for the reactions of aniline and 4-iodoaniline are neglected. A large shrinkage in the crystal structure in going from a substituted to an unsubstituted reactant, and the large size of the iodo substituent, accounts for the deviation from the Hammett's plot. Another reason for the departure of the unsubstituted reactant from the Hammett plot is the fact that it's crystal arrangement is non-centrosymmetric and has a polar axis [5] and is thus more reactive, than anticipated from it's σ value. The linearity of the Hammett plot in this reaction series shows that the rate constant obtained by the mass loss method is sensitive to the electronic changes in the aniline salt which are induced by the variation of substituents. The negative slope shows that as the electron donating power of the substituent decreases or the electron withdrawing power increases, the value for the energy of activation decreases.
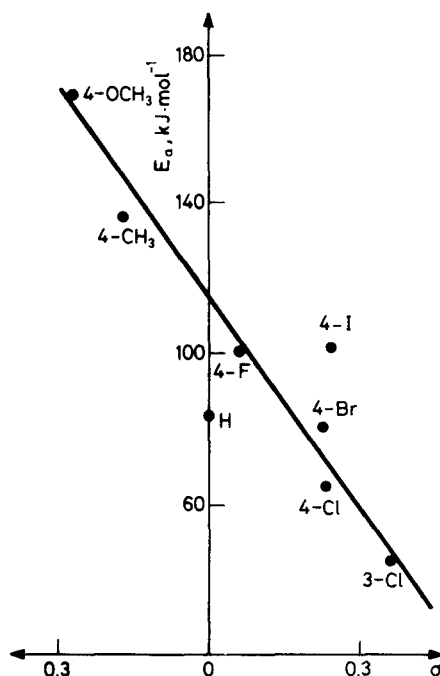

Fig. 11 Plot of Hammett' σ constant against in energy of activation for mass-loss method

The heat of addition of two molecules of gaseous amine to the anhydrous crystalline cobalt halides [12] which have been determined for some pare substituted anilines (X = H, CH_3, Cl, Br, OCH_3 etc.) are almost independent of the substituent and lie in the range (179.7–193.2 KJ mol^{-1}). The heat of addition of two moles of amine to an isolated molecule of $CoCl_2$ is 397.1 KJ mol^{-1}. A good correlation between E_a und σ shows that the processes involved in the two cases are different, i.e. in the solid-solid reactions the attachment of nitrogen to metal atom is not the rate determining process. This observation is further substantiated by the results of the reaction between solid anhydrous cobalt chloride and solid p-toluidine and p-chloroaniline. The reactions go to completion immediately on mixing at room temperature (20°) to give the aniline adducts (without the formation of a eutectic).

In order to be further sure that the Hammett equation applies exclusively to the phase-boundary process, the value of the rate constant was also determined at the initial stage of the reaction (up to $\alpha < 0.05$) at which there is no diffusion. Rate of reaction of cobalt(II) acetate with some aniline salts (X = 3-Cl, 4-Cl, 4-Br, F-F, H, 4-CH_3 and 4-OCH_3) was determined under identical conditions at 368 K. Weight loss $vs.$ time plots were analyzed by the differential mirror technique [14], in which the interference of product to inhibit or accelerate the reaction is negligible. Except for the reaction of 4-bromoaniline salt, the plot of log k_3 $vs.$ σ is linear with a correlation of 0.98 and a slope of 2.079. The value of slope by capillary technique at 368 K is 1.615(1) i.e. the effect of variation of the substituent is more prominent in the phase-boundary process than in the case in which the rate constant is governed by phase boundary processes at the initial stages and by diffusion after the completion of initial reaction.

A comparison of the energy of activation values for the reactions of cobalt acetate with aniline hydrochlorides, which have been studied by both methods reveals that the values are higher for the capillary method than for the corresponding mass-loss method. This is expected, as in mass loss method the major amount of reaction is at phase boundary and diffusion is less significant while in the latter case diffusion is more important.
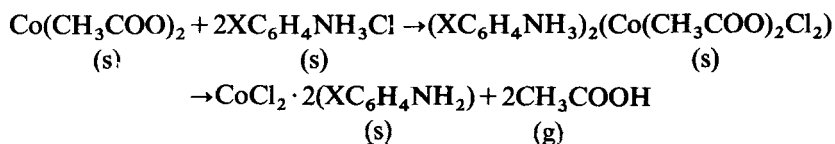
As the electron donor capacity of the substituent increases, the difference in energy of activation values by the two methods decreases, and for 4-methoxyaniline hydrochloride the values are almost comparable which shows that in this case the rate is controlled in both the methods by diffusion. The value of the reaction constant for E_a $vs.$ σ for capillary technique is -116.4 KJ mol^{-1} and by the mass loss method for the same substituents is -183.4 KJ mol^{-1} which shows that for the some series, the energy of activation is more susceptible to the electronic changes in the substituent in the mass loss method than in capillary technique.

The processes occuring at the reactant/reactant boundary may be summarized as follows:

(i) With the collapse of polymer network of cobalt acetate, Cl^- attaches to the metal. This step is complete immediately on mixing. In the reflectance spectra of freshly mixed reactants the bands due to octahedral cobalt acetate (560 nm) vanish completely and a new band (640 nm) due to tetrahedral cobalt(II) species; $(RNH_3)_2[Co(CH_3COO)Cl_2]$ is observed. This observation is also endorsed by the infrared spectra of freshly mixed reactants.

(ii) Proton is transferred from RNH_3^+ to acetate with subsequent evolution of acetic acid and attachment of nitrogen to cobalt in a concerted step as no free amine was detected in infrared spectra of freshly mixed reactants or at any later stage.

The finding that the Hammett equation holds true in this series in mass loss method as well as initial reaction rate method implies that the same chemical reaction mechanism holds good at the junction of two reactants and that the reaction path obtained independently from capillary technique [1] is true. Thus we conclude that Hammett equation applies to the (i) overall reaction which involves diffusion and phase-boundary process and (ii) phase boundary process alone. The reaction can be represented as

$$Co(CH_3COO)_2 + 2XC_6H_4NH_3Cl \rightarrow (XC_6H_4NH_3)_2(Co(CH_3COO)_2Cl_2)$$
$$\text{(s)} \qquad\qquad \text{(s)} \qquad\qquad\qquad \text{(s)}$$
$$\rightarrow CoCl_2 \cdot 2(XC_6H_4NH_2) + 2CH_3COOH$$
$$\text{(s)} \qquad\qquad \text{(g)}$$

A comparison of the rates in the solution phase will be helpful in knowing the extent of change, but since these reactions are very fast, a method for study in the solution phase has to be explored.

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Zusammenfassung — Mittels Thermoanalyse wurde die Kinetik der Festkörperreaktion zwischen Kobalt(II)azetat und substituierten Anilinhydrochloriden untersucht. Alle Reaktionen laufen vollständig ab. Die kristallinen Produkte wurden mittels physikalisch-chemischer Methoden charakterisiert. Die Aktivierungsenergie der Reaktion von Kobalt(II)azetat mit Anilin, 3- und 4-Chlor-, 4-Jod-, 4-Brom-, 4-Fluor-, 4-Methoxy- und 4-Methylanilin beträgt 83.4, 44.2, 64.2, 100.9, 79.8, 99.9, 168.7 bzw. 135.9 kJ/mol. Bei der Darstellung der Aktivierungsenergie in Abhängigkeit von der Hammettkonstante σ konnte Linearität mit einem Anstieg von -169.9 kJ/mol festgestellt werden. Die Reaktivität dieser Reaktionen wurde mittels Kapillar- und thermischen Verfahrens verglichen.

Резюме — Методом термического анализа изучена кинетика реакции между твердыми ацетатом кобальта и гидрохлоридами замещенных анилина. Все реакции проходят до конца. Образующиеся кристаллические продукты были охарактеризованы физико-химическими методами. Энергии активации реакций ацетата кобальта с гидрохлоридами анализа, 3-и 4-хлор-, 4-иод-, 4-бром-, 4-фтор-, 4-метил- и 4-метоксианилинов равнялись, соответственно, 83,4; 44,2; 64,2; 100,9; 79,8; 99,9; 135,9 и 168,7 кдж·моль⁻¹. Установлена линейная зависимость между энергиями активации и σ-константами Гамметта с угловым наклоном равным $-169,9$ кдж·моль⁻¹. Проведено сопоставление реакционной способности таких взаимодействий, установленных капиллярным методом и методом термического анализа.