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Linear-Free Energy Relationships in Solid-State Reactions

I. Reactions of Cobalt Acetate with Substituted Aniline Hydrochlorides

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Solid–solid reactions of anhydrous cobalt(II) acetate with various substituted aniline hydrochlorides have been studied. The reaction products, $CoCl_2(4\text{-}XC_6H_4NH_2)_2$, where $X = OCH_3$, CH_3, F, Br, or Cl, have been characterized. The kinetics have been studied by noting the thickness of the colored boundary of the product. The values of energy of activation are 162.3, 148.6, 120.4, 102.9, and 104.6 kJ mole^{-1} for $X = OCH_3$, CH_3, F, Br, and Cl, respectively. A plot of Hammett's constant σ versus log k is linear with values of ρ 2.321, 2.012, 1.781, and 1.615 at 353, 358, 363, and 368 K, respectively.
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Introduction

Comparative studies (*1*) are helpful in understanding the reaction mechanism, and in predicting the behavior and path of reactions not studied. The amount of work done in this field in solution is large (*2*), but there is no report of the application of the concept of linear free energy relationships in solid-state reactions. In solids, apart from many factors upon which a reaction in the fluid phase depends, the rigidity and geometry of the lattice are other important parameters to be taken into account. For correlational studies in solid–solid reaction series the crystal structure should be the same within the series as should be also the nature of the bond, so that the effect of the rigidity only on reaction rate is studied.

Bis-damine complexes of cobalt chloride have been studied extensively (*3–5*). A new technique for the preparation of these complexes in the solid state from the reaction of cobalt acetate with substituted aniline hydrochlorides is reported here. Since most of the aromatic amines are liquids at ordinary temperature, the corresponding hydrochloride salts, which are stable as solids over a considerable range of temperature, were used for these studies. Various products of the attachment of aniline and substituted derivatives of aniline to cobalt halides have the same composition $CoCl_2 \cdot 2$ amine and are also isostructural (*11*). These compounds are tetrahedral, in which the Co–N bond is predominantly covalent. Also the crystal structures of certain amine hydrochlorides (*6–7*) which have been studied are similar. Thus this solid–solid reaction series should be a very useful starting point for the study of linear-free energy relationships, when the crystal structures of reactants and products are similar and also when these do not possess a polar axis in

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the solid state. The kinetics of formation have been studied from noting the movement of the colored boundary of the products at the reactant/product interface.

Experimental

Materials. Cobalt acetate (Apex AR) was dried at 140°C for 6 hr to get the anhydrous sample. The composition was established by analyzing the sample volumetrically for cobalt (*8*). 4-Anisidine hydrochloride (CDH, AR) was used as such. Hydrochloride salts of 4-bromoaniline, 4-chloroaniline, 4-fluoroaniline, and 4-toluidine were prepared by passing dry hydrogen chloride gas in solutions of aromatic amines in alcohol and purified by recrystallization from alcohol. Purity was checked by the estimation of chlorine content by Volhard's method (*8*) and by melting points. The experimental results agree well with the expected and literature values. The compounds were sieved to a fixed mesh size, using BSS standard sieves. The products were also prepared in solution by mixing the amine and cobalt(II) chloride in ether.

Apparatus. The reflectance spectra were recorded on a VSU-2P Type spectrophotometer in the range 200–1000 nm using magnesium oxide as reference material. Infrared spectra were run on a SP3-300 Pye-Unichem instrument in a potassium bromide matrix in the range 200–4000 cm^{-1}. Magnetic moment studies were done on a Guoy balance. X-Ray diffractograms were obtained by using a PW 1720 X-ray generator with a Debye–Scherer camera. Thin layer chromatography was done using benzene–methanol (95 : 5) as eluent.

Kinetics. The color of the products formed varies from light to dark blue which can be distinctly differentiated from that of the reactants. The kinetics were therefore studied by measuring the thickness of the colored boundary as a function of time, at 353, 358, 363, and 368 K by the capillary technique first used by Rastogi *et al.* (*9*). Glass capillaries of inner diameter 0.3 cm and a travelling microscope with least count of 0.002 cm were used for these studies. Cobalt acetate (<42 μm) and substituted aniline hydrochlorides (60 μm) were used for the kinetic studies. Each experiment was reported thrice to check the reliability of the data.

Results and Discussion

The solid–solid reactions of cobalt acetate with substituted aniline salts give products of stoichiometry $Co(4\text{-}XC_6H_4NH_2)_2Cl_2$ where $X = OCH_3$, CH_3, F, Br, and Cl. In the reaction, the nitrogen of the amine becomes coordinated to the metal atom with the evolution of acetic acid. All the amines act as unidentate ligands.

The structures of the products have been ascertained from various spectral and analytical measurements. The products were analyzed for Co, Cl, C, H, and N and the results of these elemental analyses support the stoichiometry as $Co(XC_6H_4NH_2)_2Cl_2$.

In infrared spectra, salts of primary amines show strong, broad absorption between 3000 and 2500 cm^{-1} arising from the asymmetric and symmetric stretches in the NH_3^+ group. In addition, multiple combination bands of medium intensity occur in the 2800–2000 cm^{-1} region. Free primary amines exhibit N–H stretching vibrations near 3500 cm^{-1}, but in compounds in which a primary amine is coordinated to a metal atom the N–H band shifts to 3300 cm^{-1}. The IR spectra of the solid-state reaction products (Table I) has absorption between 3300 and 3200 cm^{-1} assignable to a coordinated primary amine and has no bands due to a NH_3^+ group. The reflectance spectra show only one absorption in the visible region at about 15000 cm^{-1} ($4_{A_2} \rightarrow 4_{T_1(P)}$). The magnetic moment values for the complexes lie in the range 4.4–4.8 Bohr magnetons (B.M.) which are typical for tetrahedral co-

TABLE I

ELEMENTAL, REFLECTANCE, INFRARED AND MAGNETIC MOMENT DATA FOR THE SOLID-STATE REACTION PRODUCTS OF COBALT(II) ACETATE WITH SUBSTITUTED ANILINE HYDROCHLORIDES

Substituent	Elemental composition (%)					μ_{eff} (B.M.)	λ (cm^{-1})	ν_{max} (cm^{-1})
	C	H	N	Co	Cl			
p-Cl	36.30	3.06	6.50	15.90	19.63	4.50	15625(s)[a]	3300(m)[a]
	(37.40)[a]	(3.17)	(7.27)	(15.32)	(18.44)			3255(m)
p-Br	29.02	2.28	6.05	12.70	15.33	4.60	15625(s)	3285(m)
	(30.38)	(2.53)	(5.91)	(12.45)	(14.98)			3240(m)
p-F	40.23	3.24	8.09	16.72	19.98	4.72	15750(s)	3280(m)
	(40.91)	(3.41)	(7.95)	(16.76)	(20.17)			3230(m)
p-CH_3	47.60	5.01	8.30	16.77	20.97	4.60	15625(s)	3280(m)
	(48.84)	(5.23)	(8.14)	(17.15)	(20.64)			3235(m)
p-OCH_3	43.60	4.65	7.00	14.83	19.67	4.65	15625(s)	3270(m)
	(44.65)	(4.78)	(7.44)	(15.68)	(18.87)			3225(m)

[a] s = strong, m = medium. Values within braces are the calculated ones.

balt(II) complexes. X-Ray powder patterns of the solid and solution products are exactly identical. The *d* values are in complete correspondence with the solid and solution products. The TLC of the solid and solution products shows the presence of single components in solid phase products and the R_f values are identical with those of solution products. These observations show that the reaction goes to completion and that pure compounds are formed.

The kinetic data for the reactions show that the phase-boundary processes are very rapid so that the equilibrium is established at the boundary during the entire course of the reaction. The rate at which gaseous acetic acid is evolved at the reaction center is very slow and remains isothermal. The gaseous products diffuse away from the reaction zone along the sides of the capillary tubes and the voids between the reactants.

The kinetic data for the reactions obey the rate law

$$\xi^2 = kt + C \qquad (1)$$

where ξ is the thickness of the colored product layer at time t, and k and c are constants. The plot of ξ^2 vs t is linear, which indicates that diffusion of one of the species through the product layer is rate-determining. The diffusing species is the hydrochloride salt. This has been ascertained by separate experiments in which the position of the boundary was marked, and the direction of growth of the colored boundary was observed. With time a blue boundary developed in the direction of co-

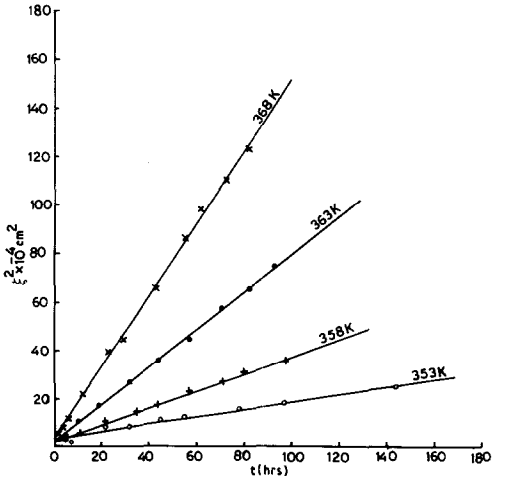

FIG. 1. Kinetic data for the reaction between $Co(CH_3COO)_2$ and 4-$OCH_3C_6H_4NH_2HCl$ at different temperatures.

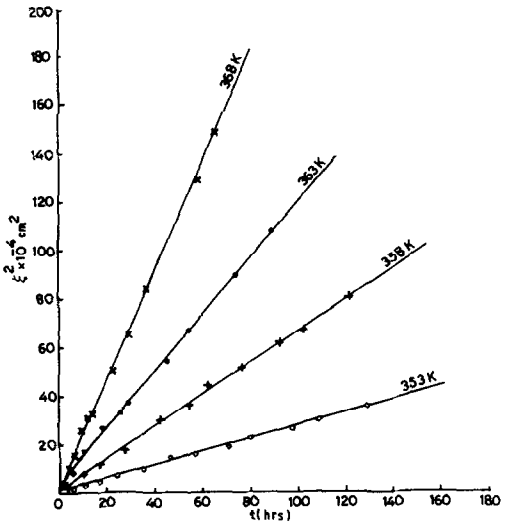

FIG. 2. Kinetic data for the reaction between $Co(CH_3COO)_2$ and 4-$CH_3C_6H_4NH_2HCl$ at different temperatures.

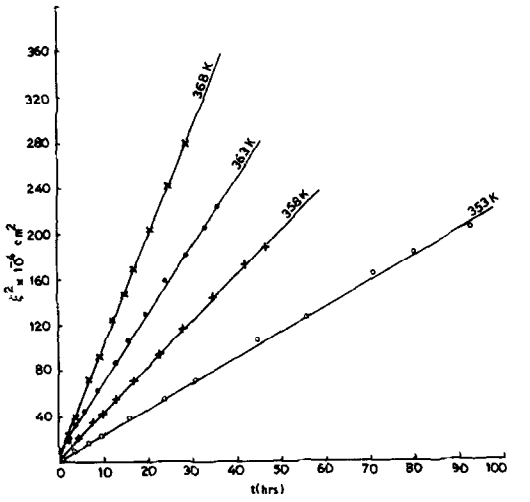

FIG. 4. Kinetic data for the reaction between $Co(CH_3COO)_2$ and 4-$ClC_6H_4NH_2HCl$ at different temperatures.

balt acetate. Cl^-, being small and symmetrical, will diffuse ahead of RNH_3^+ which is bulky; hence its diffusion should be the rate-controlling step. Results for different reactions are given in Figs. 1–5. The values of energy of activation for these reactions calculated from Arrhenius plots are 162.3, 148.6, 120.4, 102.9, and 104.6 kJ $mole^{-1}$ for $X = OCH_3$, CH_3, F, Br, and Cl, respectively.

The Hammett equation has been extensively employed to correlate the influence

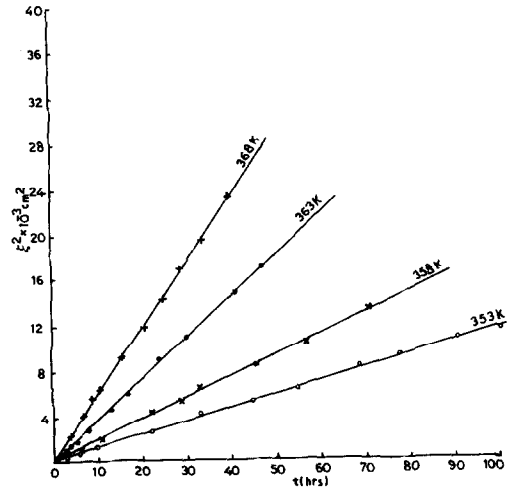

FIG. 3. Kinetic data for the reaction between $Co(CH_3COO)_2$ and 4-$FC_6H_4NH_2HCl$ at different temperatures.

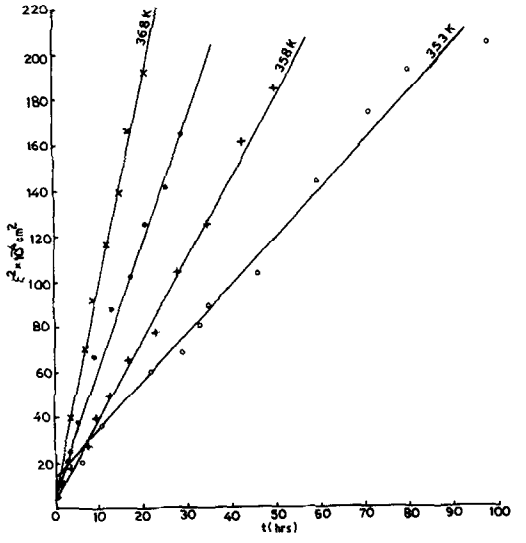

FIG. 5. Kinetic data for the reaction between $Co(CH_3COO)_2$ and 4-$BrC_6H_4NH_2HCl$ at different temperatures.

of substituents on the reactivity of substrates containing aromatic groups. Such studies throw considerable light on the mechanisms of reaction in the solution phase. Recently the kinetics (*12*) of thermal decomposition of aniline, 4-chloroaniline, and 4-methylaniline have been studied in benzene solution. Linear correlations were found between the rate constants and activation energies of thermal decomposition and the Hammett substituent constants. Linear correlations (*13*) have also been observed for heat of dissociation of hydrochlorides of aniline and 2-, 3-, and 4-chloroaniline with Hammett constants. However, there is no report of such correlation of any property with a substituent parameter for the solid-state reactions. To see the applicability of Hammett's equation in these reactions, the following constants are chosen: σ, Hammett's constant which is a measure of the combined inductive and mesomeric influence of the substituent on the reaction; σ_I, Taft's purely inductive parameter which denotes the influence of the substituent on the reaction center by an inductive effect; and σ_R, the pure resonance parameter which measures the electromeric influence of the substituent. Values for these parameters were obtained from the literature (*1*). The plots of these constants vs log k were subjected to linear regression analysis and the results are given in Table

TABLE II

VALUES OF REACTION CONSTANT ρ AND CORRELATION COEFFICIENTS FROM LINEAR REGRESSION ANALYSIS OF σ, σ_I, AND σ_R VERSUS log k

	σ		σ_I		σ_R	
T (K)	ρ	Corr. coeff.	ρ	Corr. coeff.	ρ	Corr. coeff.
353	2.321	0.99	1.717	0.76	0.133	0.06
358	2.012	0.99	1.400	0.71	0.249	0.12
363	1.781	0.99	1.900	0.77	0.075	0.04
368	1.615	0.99	1.180	0.75	0.115	0.07

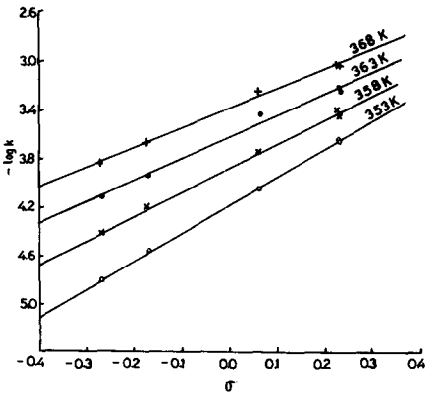

FIG. 6. Plot of Hammett's σ constant vs log k for the solid-state reaction of cobalt(II) acetate with aniline hydrochlorides.

II. It is seen that correlation for σ_R with log k is very very poor, i.e., there is very little or no contribution from resonance in the transmission of substituent electronic effects to the reaction center. The correlation of σ_I is better which means that the substituent influences the properties of the reacting molecule by inductive withdrawal of electrons to a certain extent. However, best results are obtained with σ at all temperatures, i.e., the substituent acts both by resonance and inductive effects. The best picture can be obtained by considering their combined effect on the reaction center. Plots of σ vs log k at different temperatures are given in Fig. 6. The validity of the Hammett plot shows that the reaction mechanism is same within the series.

The sign and magnitude of ρ can give us valuable information regarding the reaction characteristics. ρ is positive for nucleophilic reactions, when the benzene derivative is the substrate (*10*). ρ is greater than 1 at all temperatures, and also decreases with temperature which indicates greater electronic effects of the substituent at the reaction center.

The following observations are noteworthy to understand the phase boundary processes in the reported reaction series:

(i) The heats of addition of two molecules of gaseous amines to the anhydrous crystalline cobalt halides have been determined (*11*) and are almost independent of the substituents in the benzene nucleus of aniline. These values lie in the range 179.7–193.2 kJ $mole^{-1}$ for the *para* substituents viz., X = H, CH_3, Cl, Br, OCH_3, etc. These results indicate a predominant covalency of the Co–N bond. The heat of addition of two moles of amine to an isolated molecule of $CoCl_2$ is approximately 397.1 kJ $mole^{-1}$.

(ii) The solid–solid reaction of cobalt chloride with amine was also investigated. For example, the reaction of cobalt chloride with *p*-toluidine is instantaneous and is complete immediately, on mixing, to give the addition product.

Observations (i) and (ii) show that rates for the coordination of nitrogen to cobalt(II) are of the same order, but very fast.

(iii) Reflectance spectra of freshly mixed components in these reactions show the presence of tetrahedral Co(II) species. Infrared spectra of freshly mixed reactants have bands corresponding to the presence of the RNH_3^+ group.

Thus, consequently upon the diffusion of $RNH_3^+Cl^-$ through the product layer, a sequence of following chemical processes occurs at the product/Co(II) acetate boundary:

(i) The polymeric structure of cobalt(II) acetate breaks and Cl^- is attached to Co(II).

(ii) Proton transfer takes place from RNH_3^+ to acetate to form and then evolve acetic acid.

(iii) One nitrogen is coordinated to Co(II) through its lone pair of electrons and then the second in the same manner.

Processes (ii) and (iii) may occur simultaneously. Schematically the reaction may be represented as follows:

$$\underset{(s)}{Co(CH_3COO)_2} + \underset{(s)}{2XC_6H_4NH_3^+Cl^-} \rightarrow$$

$$[(XC_6H_4NH_3)_2^+(Co(CH_3COO)_2Cl_2)^{2-}] \rightarrow$$

$$\underset{(s)}{Co(XC_6H_4NH_2)_2Cl_2} + \underset{(g)}{2CH_3COOH}$$

These results account for the linearity of the Hammett's plot. It is thus concluded that the linear free energy relationships may apply even in the solid state provided the reactants in the series are (i) isomorphous, (ii) have similar bonding, and (iii) have no polar axis in the solid. Work with reactants in which any of the above characteristics change is in progress.

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References

1. N. B. CHAPMAN AND J. SHORTER (Eds.), "Advances in Linear Free Energy relationships, Plenum, New York (1972).
2. C. V. SENÖFF, *Coordination Chem. Rev.* **32,** 111 (1980).
3. I. S. MASLENNIKOVA, *Zh. Fiz. Khim.* **51,** 2088 (1977).
4. ROBIN H. CLARK AND CHARLES S. WILLIAMS, *Inorg. Chem.* **4,** 350 (1965).
5. T. I. MALINOVSKI I, *Soviet Phys. Crystallogr. (Engl. Transl.)* **2,** 723 (1957).
6. M. COLAPIETRO, A. DOMENICANO, C. MARCIANTE, AND G. PORTALONE, *Acta Crystallogr. B* **37,** 387 (1981).
7. M. COLAPIETRO, A. DOMENICANO, AND G. PORTALONE, *Acta Crystallogr. B* **38,** 2825 (1982).
8. A. I. VOGEL, "A Text Book of Quantitative Inorganic Analysis" Longman, London (1975).
9. R. P. RASTOGI, P. S. BASSI, AND S. L. CHADHA, *J. Phys. Chem.* **67,** 2569 (1963).
10. P. R. WELLS, "Linear Free Energy Relationships," Academic Press, New York/London (1968).
11. A. V. ABLOV AND TS. B. KONUNOVA, *Zh. Neorg. Khim.* **8,** 1122 (1963); A. V. ABLOV, TS. B. KONUNOVA-FRID, AND V. A. PALKIN, *Zh. Neorg. Khim.* **5,** 1544 (1960).
12. B. M. TSIGIN, I. I. KONSTANTINOV, AND YU. M. GUSEV, *Zh. Prikl. Khim.* **50,** 499 (1977).
13. I. I. KONSTANTINOV, V. D. SELIVANOV AND T. I. MELENT'EVA, *Zh. Fiz. Khim.* **49,** 1058 (1975).