Journal of Themal Analysis, Vol. 34 (1988) 723–732

SOLID STATE REACTIVITY OF ORGANIC COMPOUNDS WITH INORGANIC COMPOUNDS II.

Reactions of cobalt acetate with aniline hydrobromides

P. S. Bassi, G. S. Chopra* and *R. Prasher*

DEPARTMENT OF CHEMISTRY, GURU NANAK DEV UNIVERSITY,
AMRITSAR-143005, INDIA

(Received March 7, 1987; in revised form July 30, 1987)

Cobalt acetate reacts with aniline, 2-, 3- and 4-chloroanilinehydrobromides in the solid state to give the products $CoBr_2 . 2$ amine in which the acetate is replaced by bromide and the amine gets attached to the metal in a concerted step. The products have been identified by elemental, spectral and thermoanalytical methods. The kinetics of these reactions have been studied by the mass loss method. The values of energy of activation are 142.0, 41.0, 77.0 and 71.4 kJ mol^{-1}. The greater reactivity of 2-chloro is due to ortho effect. An intermediate adduct $(RNH_3)_2(Co(CH_3COO)_2Br_2)$ has also been characterized.

Studies in solid-solid reactions between organic solids and inorganic solids are far and few [1]. The present investigations describe the reactions between cobalt acetate and a series of substituted aniline hydrobromides. In the reactions, topochemical factors do not play much role, as these reactions occur in powders and also because incoherent products are formed over reactants. The purpose of this study was to see the effect on kinetics of adding and also changing the position of substituent, i.e. Cl in the benzene ring.

In previous communications we have reported the study of solid-solid reactions of aniline hydrochlorides with cobalt acetate by capillary technique [2], by mass loss method [3] and with zinc acetate by mass loss method [4]. In all these reactions the products formed are $MCl_2 \cdot 2$ amine; M = Co, Zn and the reactions proceed by the formation of an intermediate adduct. The composition of various products of attachment of anilines to cobalt bromide is same viz $CoBr_2 \cdot 2$ amine. The products are tetrahedral in which the Co—N is predominantly covalent [5].

---

* Author to whom all correspondence should be directed.

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

Experimental

Cobalt acetate (AR) was dried at 413 K for six hours to get the anhydrous sample. The sample was titrimetrically analyzed for cobalt [6]. % found 32.9 (calcd. 33.3). Aniline, 2-, 3- and 4-chloroaniline hydrobromides were prepared by passing dry hydrogenbromide gas in ethereal solutions of the amines. The salts were purified by recrystallisation from alcohol. The bromide content of the salts was determined by Volhard method and is given in Table 1. The compounds were sieved using Geosyn sieves and particles of size 44 ± 2 μ of aniline salts and cobalt acetate were collected and dried at 393 K for experimental studies.

The reflectance spectra studies were done a Shimadzu Grapicord UV–240 instrument with barium sulphate as the reference material. The infrared spectral studies were done on a SP3–300 Pye Unichem instrument in potassium bromide in the region 4000–200 cm^{-1}. TG, DTA and DTG were recorded on a Stanton Redcroft (STA–780) model at a heating rate of 10 deg min^{-1} in nitrogen atmosphere using about 10–15 mg sample for each run. Thin layer chromatography was done in benzene-methanol (95 : 5) mixture as the eluent. Kinetics were studied by the mass loss method in which 0.001 moles of cobalt acetate were mixed with aniline salts (0.002 moles) in a bucket and suspended in a thermostat (±0.2 K). The bucket was attached to an electrical balance (±0.01 mg) with a platinum wire. Change in weight was recorded with time and each reported measurement is a mean of three runs. For obtaining solution phase reaction products, anhydrous cobalt bromide was refluxed with excess of amine in ether.

Results and discussion

Solid-solid reactions of cobalt acetate with substituted aniline hydrobromides give bis(aniline) cobalt(II) bromide complexes according to the stoichiometric equation:

$$\underset{(s)}{Co(CH_3COO)_2} + \underset{(s)}{2XC_6H_4NH_3Br} \rightarrow \underset{(s)}{CoBr_2 \cdot 2(XC_6H_4NH_2)} + \underset{(g)}{2CH_3COOH}$$

where X = H, 2-Cl, 3-Cl and 4-Cl.

In these reactions the acetate is replaced by bromide with the evolution of gaseous acetic acid. The proton exchange occurs in favour of acetic acid ($p$ka = 4.74) because of the greater acidity of the anilines ($p$ka = 4.63, 2.65, 3.46 and 4.15 for X = H, 2-Cl, 3-Cl and 4-Cl respectively). Acetic acid has been identified to be the only gaseous product from its characteristic smell and the following tests. The evolved gas was passed through water using nitrogen as carrier

Table 1 Elemental, spectral and TLC data for the reactants and products obtained both from solid and solution phase reactions

Compound	Product obtained from	Co, %	Br, %	Infrared spectra, cm^{-1}					Reflectance TLC, nm	
				ν_{asym} NH_2	ν_{sym} NH_2	$\nu_{N-H\cdots X}$	ν_{Co-N}	ν_{Co-Br}	λ_{max}	Rf
$2\text{-}ClC_6H_4NH_3Br$		—	40.0	2840	2600	—	—	—	—	—
$CoBr_2 \cdot 2(2\text{-}ClC_6H_4NH_2)$	Solid	13.4	33.4	3270	3220	3120	420, 380	320,305	660	0.42
	Solution	13.0	33.6	3290	3230	3130	410	310	660	0.42
$3\text{-}ClC_6H_4NH_3Br$		—	40.2	2850	2570	—	—	—	—	—
$CoBr_2 \cdot 2(3\text{-}ClC_6H_4NH_2)$	Solid	13.0	33.0	3260	3210	3120	420, 390	280	659	0.50
	Solution	13.0	33.2	3270	3220	3120	420, 395	280	660	0.50
$4\text{-}ClC_6H_4NH_3Br$		—	40.3	2870	2540	—	—	—	—	—
$CoBr_2 \cdot 2(4\text{-}ClC_6H_4NH_2)$	Solid	13.2	33.1	3290	3240	3140	420	300	660	0.44
	Solution	13.1	33.1	3290	3240	3140	425	310	660	0.43
$C_6H_5NH_3Br$		—	46.1	2900	2600	—	—	—	—	—
$CoBr_2 \cdot 2(C_6H_5NH_2)$	Solid	15.1	39.2	3260	3220	3120	410, 350	290	660	0.39
	Solution	15.0	38.8	3280	3230	3140	425, 365	305	659	0.39

gas. The solution was concentrated and to it was added methanol and sulfuric acid. Upon heating the mixture gave distinct fruity odour smell. No other gas was detected after testing for hydrogen halides (silver nitrate), carbon dioxide (lime water) and water (anhydrous copper sulphate). The solid and solution phase reaction products were analysed for their Co and Br contents (Table 1). The total loss in weight was measured after mixing the reactants stoichiometrically. The loss corresponds to the elimination of two moles of gaseous acetic acid. These results agree with the formulation $CoBr_2 \cdot 2(XC_6H_4NH_2)$ for the products.

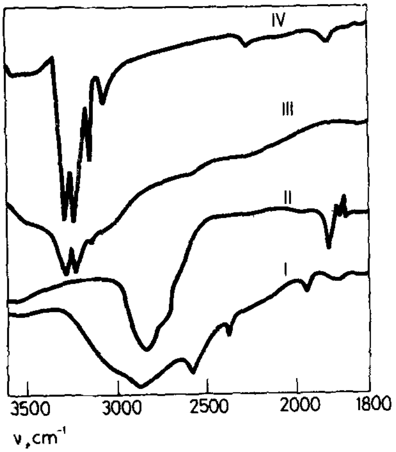

Fig. 1 IR spectra of $Co(CH_3COO)_2 + C_6H_5NH_3Br$ system

The reflectance spectra of solid products obtained from solid and solution phase reactions show only one absorption in the visible region at 640 nm due to tetrahedral Co(II) species. The spectra of freshly mixed components show a broad band from 600–650 nm and the band due to octahedral cobalt acetate (560 nm) is absent, i.e. complete change in coordination to tetrahedral form occurs immediately on mixing. The spectra for the solid and solution phase products are identical. The infrared spectra of a number of complexes $CoBr_2 \cdot 2$ amine that have been reported in literature [7], exhibit asymmetrical and symmetrical ν_{NH_2} at 3300 and 3200 cm^{-1} respectively. The spectra of the products obtained after heating the 1:2 stoichiometric mixture in a thermostat show a sharp blue shift of the symmetric and asymmetric stretching from 2800 to 3300 cm^{-1} as compared to the aniline salts. The disappearance of the $\nu_{NH_3^+}$ confirms the completion of the reaction. Co—N and Co—Br bands appear at 380–400 and 290–310 cm^{-1}. Figure 1 shows IR spectra for aniline hydrobromide-cobalt acetate system. Aniline hydrobromide (I) absorbs at 2900 and 2600 cm^{-1}. The solid phase product (IV) absorbs at 3260 and 3220 cm^{-1} and the solution phase product (III) at 3280 and 3230 cm^{-1} respectively. The spectra of the fresh mixture (II) has a broad band at 2800 cm^{-1}. There are no bands above 3000 cm^{-1} which shows the absence of free or coordinated NH_2 groups in the fresh mixtures.

The solid-solid reactions go to completion and only single products are formed. There are no impurities of the reactants left in the product. Thin layer chromatography of the products show that single spot compounds are formed. The Rf values for the solid phase and solution phase products are same (Table 1).

The reaction of 4-chloroaniline hydrobromide with cobalt acetate was also studied by heating fresh mixture of the reactants directly in a simultaneous thermal analyzer. The thermal decomposition curves of cobalt acetate and aniline hydrobromides were obtained to compare their thermal behaviour with that of the stoichiometric mixtures. Cobalt acetate shows a weak endotherm above 450 K due to loss of small amount of water ($\sim 3\%$) and then decomposes. 4-chloroaniline hydrobromide shows no change below 470 K. The DTA of fresh mixture (Fig. 2) exhibits three endothermic effects at 380, 425 and at 460 K. The TG shows loss in the range 350–415 (22%) and 415–465 K (9%) followed by decomposition at higher temperature. The first step corresponds to the loss of two acetic acid molecules (calcd. 20%) from the mixture. As there is no peak in the DTA of the reactants up to 450 K, the result suggests that solid state interaction occurs in the temperature range 350–410 K. The adduct formed then decomposes.

Kinetics

The kinetics of the reactions of cobalt acetate with aniline, 2-, 3- and 4-chloroaniline hydrobromides have been studied by measuring the weight loss in mixtures of cobalt acetate with aniline salts of fixed particle size (44 ± 2 μ) at different temperatures. As seen from the stoichiometric equation acetic acid is the only gaseous reaction product. With the progress of reaction, the amount of gaseous acetic acid evolved increases with time and this is studied by measuring the change in weight of the mixtures. The results are given in Figs 3–6. No-obedience of the linear plot for all reactions throughout the entire range shows that phase boundary processes alone are not significant and other phenomenon e.g. diffusion also plays a role in these reactions. The kinetic results were further analysed for various solid state reaction models by computer to test if any single model (at least experimentally) operates in all reactions. Best fit was obtained for $\log \alpha$ *vs.* $\log t$ plots in the equation $\alpha^n = kt$, where α is the fraction of reaction at time t and n and k are constants. The activation energies were obtained from Arrhenius plot (Table 2).

The unsubstituted aniline salt is the least reactive. Electron withdrawing chloro substituents enhance the reactivity by decreasing the electron density at nitrogen, thereby facilitating the transfer of acidic proton from NH_3^+ to acetate. In an aromatic ring electron donors disperse the positive charge of the anilium ion and thus stabilizes the ion relative to the amine. Electron withdrawal tends to intensify the positive charge of the anilium ion, and thus destabilizes the ion relative to the

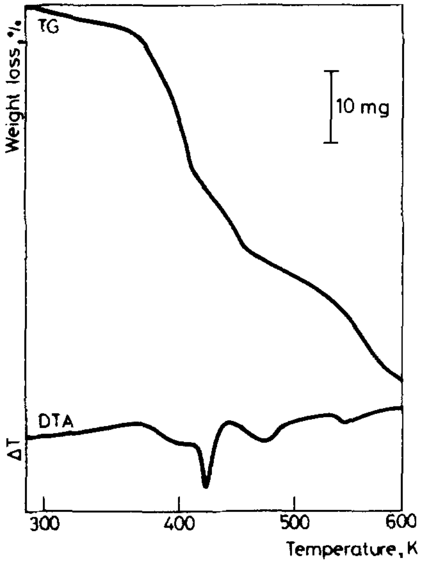

Fig. 2 TG–DTA of $Co(CH_3COO)_2 + 4\text{-}ClC_6H_4NH_3Br$ system

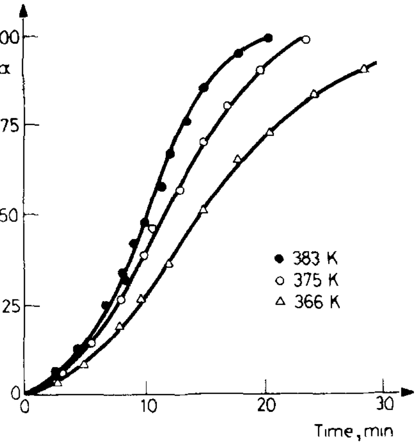

Fig. 3 Kinetic data for the reaction between $Co(CH_3COO)_2$ and $2\text{-}ClC_6H_4NH_3Br$

amine. The greater acidity of 2-chloro compound is due to the ortho effect. Even electron releasing substituents enhance acidity when they are ortho to the amino group and electron withdrawing substituents do so to a much greater extent from the ortho position than from the meta or para position.

The solid-solid reaction of anhydrous cobalt bromide with 4-chloro aniline (only amine that is solid at room temperature out of the ones used in the present studies) was also investigated. The reaction is very fast and the adduct is formed instantaneously. The nature of the product was established by spectral methods. Reaction of cobalt acetate with 4-chloroaniline also takes place instantaneously to

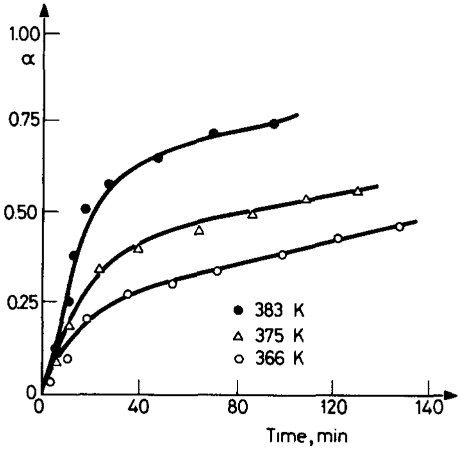

Fig. 4 Kinetic data for the reaction between $Co(CH_3COO)_2$ and $3\text{-}ClC_6H_4NH_3Br$

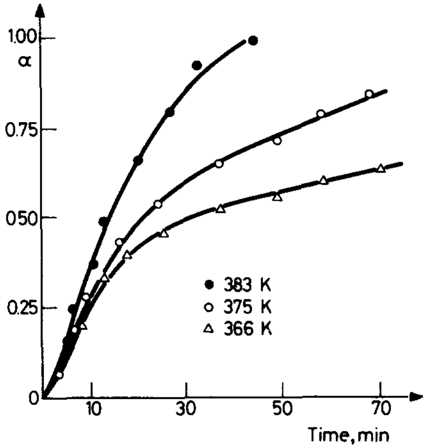

Fig. 5 Kinetic data for the reaction between $Co(CH_3COO)_2 + 4\text{-}ClC_6H_4NH_3Br$

give $Co(CH_3COO)_2 \cdot 2(4\text{-}ClC_6H_4NH_2)$. The product is octahedral in which nitrogen is coordinated to the metal as shown by reflectance and IR spectra.

Heats of addition of various aniline derivatives to anhydrous cobalt halides have been reported in literature. The heats are independent of the aromatic amine, despite the fact that the amines differ in their electric moments and in the group moments of the substituents [5]. The energy liberated as a result of addition of the amines to cobalt bromide comes chiefly from the formation of Co—N bond. The values of heat of incorporation of gaseous aniline, 3- and 4-chloro aniline in the lattice of $CoBr_2$ were found to be 186.8, 194.8 and 194.8 J mol^{-1} respectively. It was found that the difference is very small when one substituent is replaced by another. These results show that the attachment of free nitrogen of aniline to cobalt is a highly favoured process and is complete immediately on mixing even in the solid state and that this process is independent of the nature of the amine as evidenced by the studies in the solution phase.

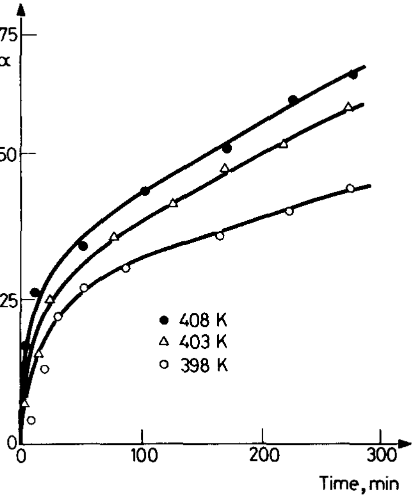

Fig. 6 Kinetic data for the reaction between $Co(CH_3COO)_2 + C_6H_5NH_3Br$

The reflectance spectra of the freshly mixed reactants show bands only due to tetrahedrally bound cobalt(II) (640 nm) and no bands due to octahedrally bound cobalt (560 nm). The IR of freshly mixed reactants shows the absence of any bands due to RNH_3^+ and due to coordinated or free NH_2. This indicates the formation of an intermediate $(RNH_3)_2[Co(CH_3COO)_2Br_2]$ prior to the transfer of proton from the amine salt to the acetate. The coordination of amino nitrogen takes place simultaneously, once the proton is transferred.

Reactions of cobalt acetate with aniline, 2-, 3- and 4-chloroaniline hydrochlorides have already been reported (Table 2). The reactions with bromide salts are comparatively slower. This may be because of the larger size of bromide which decreases effective contact between the reactants and also would slow down the effective penetration of the reactant through the product lattice with the progress of the reaction. It has been shown in the case of reactions of cobalt acetate with aniline hydrochlorides in the capillary technique that the diffusing species is the aniline salt [2], hence the smaller size of chloride permits better contact and greater diffusivity through the product lattice.

Table 2 Energy of activation values for reactions of cobalt acetate with aniline salts

Substituent	Hydrobromides, kJ mol^{-1}	Hydrochlorides,[a] kJ mol^{-1}
H	142.0	83.4
2-chloro	41.0	35.0
3-chloro	77.0	44.2
4-chloro	70.4	64.2

[a] from [3].

References

1 P. S. Bassi and G. S. Chopra, J. Solid State Chem., 62 (1986) 253.
2 P. S. Bassi and G. S. Chopra, J. Solid State Chem., 61 (1986) 103.
3 P. S. Bassi and G. S. Chopra, J. Thermal Anal. (in press).
4 P. S. Bassi and G. S. Chopra, J. Indian Chem. Soc. (in press).
5 A. V. Ablov and Ts. B. Konunova, Russ. J. Inorg. Chem., 8 (1963) 582.
6 A. I. Vogel, A textbook of Quantitative Inorganic Analysis, Fourth edition, ELBS and Longman, London 1982, p. 609.
7 A. V. Ablov, N. N. Proskina and L. F. Chapurina, Zh. Neorg. Khim., 10 (1965) 1350.

Zusammenfassung — In einer Reaktion von Kobaltazetat mit Anilin, 2-, 3- bzw. 4-Chloranilinhydrobromid im festen Zustand wird in einem Schritt das Azetat durch das Bromid ersetzt und gleichzeitig das Amin an das Metall gebunden. Als Ergebnis dessen wird $CoBr_2 \cdot 2$Amin gebildet. Die Produkte wurden durch Elementaranalyse sowie spektroskopische und thermoanalytische Methoden identifiziert. Die kinetischen Eigenschaften dieser Reaktionen wurden an Hand des Masseverlustes untersucht. Die Werte für die Aktivierungsenergien betragen 142,0, 41,0, 77,0 und 71,4 kJ·mol^{-1}. Für die größere Aktivität der 2-Chlor-Verbindung ist der Orthoeffekt verantwortlich. Das als Zwischenprodukt aufgetretene Addukt $(RNH_3)_2(Co(CH_3COO)_2Br_2)$ wurde ebenfalls beschrieben.

Резюме — Ацетат кобальта реагирует в твердом состоянии с гидробромидами анилина, 2-, 3- и 4-хлоранилинами, давая продукты $CoBr_2 \cdot 2$амин и в которых ацетат замещается на бром с одновременным присоединением амина к металлу. Продукты реакции идентифицированы элементным анализом, спектральным и термоаналитическим методом. Методом потери веса изучена кинетика протекающих реакций. Значения энергии активации были равными 142,0; 41,0; 77,0 и 71,4 кдж·моль$^{-1}$. Более высокая реакционная способность 2-хлоранилина обусловлена орто-эффектом. Охарактеризован также промежуточный аддукт $(RNH_3)_2(Co(CH_3COO)_2Br_2)$.