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Metal-Complex-Catalyzed Isomerization of Anils

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Exchange between the nonequivalent isopropylidene methyl groups of *N*-isopropylideneanilines is catalyzed by zinc(II) complexes of thiourea. The rates of the catalyzed exchange processes have been studied by using spin-saturation-transfer (double resonance) proton magnetic resonance. The observed rates are compared with those for anil hydrolysis and transimination by using the same catalysts. In contrast to the mechanism of the uncatalyzed isomerization, rotation about the carbon–nitrogen bond rather than inversion about the nitrogen determines the rate of the catalyzed isomerization. It seems likely that the participation of a nucleophile is also necessary to accomplish isomerization. The activation energy for catalyzed isomerization is 13 ± 2 kcal as opposed to 22 ± 2 kcal for the uncatalyzed reaction.

Introduction

Reactions involving nucleophilic attack on carbonyl or imine groups are very commonly catalyzed by acids[1] and by metal ions.[2-7] It is generally accepted that in the latter case coordination of carbonyl oxygen or imine nitrogen to the metal ion is a necessary prerequisite for catalysis. In aqueous solution the ketone or imine has to compete with a very large excess of water for a position in the coordination sphere of the metal ion. Since water is a preferred ligand, this factor limits the effectiveness of metal ions as catalysts. The use of labile metal complexes as catalysts in nonaqueous solution is therefore suggested. We have found[8-10] that a number of simple reactions of ketones and anils are effectively catalyzed by cobalt and zinc complexes of thiourea in acetone or acetonitrile solutions and have investigated the mechanisms of these reactions. In the present paper we consider the catalyzed isomerization of anils and its relationship to catalyzed anil hydrolysis and transimination reactions.
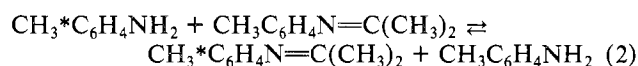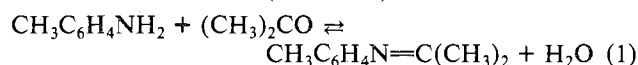
It has been shown that a metal complex such as cobalt(II) or zinc(II) tetrakis(thiourea) perchlorate effectively catalyzes the hydrolysis (or the formation) of the acetone anil of *p*-toluidine in acetonitrile.[8] A typical reaction mixture contains the following chemical species: I, *p*-toluidine; II, *N*-isopropylidene-*p*-toluidine; III, acetone; IV, water; V, catalyst—zinc(II) tetrakis(thiourea) perchlorate; VI, thiourea; VII, toluidine complexed to Zn(II); VIII, *N*-isoipropylidene-*p*-toluidine complexed to Zn(II); IX, acetone complexed to Zn(II); X, water complexed to Zn(II).

In such a system the following rates can be measured or estimated and (where appropriate) compared with the rates of the same reactions in the absence of metal complex (all of the measurements involve NMR techniques): (a) the rate of disappearance of the isopropylidene methyl peaks of II and the corresponding rate of appearance of the acetone ^{1}H NMR resonance (III); (b) the rate of exchange between the toluidine methyl resonance and the corresponding methyl group of II; (c) the rate of exchange between the NH$_2$ protons of *p*-toluidine and water (IV); (d) the rate of exchange between the two nonequivalent methyl groups (A and B) of II; (e) the rate of exchange between the water (hydrogen or deuterium) and the methyl hydrogens of III and IV; (f) the rate of exchange between free thiourea (VI) and complexed thiourea (tu) V; (g) the rate of exchange between free toluidine (I) and complexed toluidine (VII); (h) the rate of exchange between

II
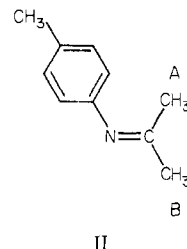
free anil (II) and complexed anil (VIII); (i) the rate of exchange between water (IV) and complexed water (X).

Processes a–d are all metal complex catalyzed with process a, for example, being faster[8] than the uncatalyzed reaction by a factor of up to 10^6. Exchange reaction b is faster[9] than a by a factor of approximately 10^2. This implies that in (a) anil formation or hydrolysis (reaction 1) is being measured but (b) involves transimination (reaction 2) which is faster.

$$CH_3C_6H_4NH_2 + (CH_3)_2CO \rightleftharpoons CH_3C_6H_4N=C(CH_3)_2 + H_2O \quad (1)$$

$$CH_3{}^*C_6H_4NH_2 + CH_3C_6H_4N=C(CH_3)_2 \rightleftharpoons CH_3{}^*C_6H_4N=C(CH_3)_2 + CH_3C_6H_4NH_2 \quad (2)$$

Catalyzed transimination involving two different substituted anilines has also been demonstrated.[9] The ligand exchange reactions (f)–(i) are all fast on the NMR time scale at room temperature (for paramagnetic Co(tu)$_4{}^{2+}$) and cannot be the rate-determining steps for either reaction 1 or reaction 2. Reaction c is slow in the absence of catalyst but rapid on the NMR time scale even at −60 °C with catalyst present. Proton-transfer steps cannot therefore be rate determining as is confirmed by kinetic isotopic measurements. Reaction e is considerably slower than (a) or (b) in the presence of catalyst, indicating that enolization of the ketone is not involved in the mechanism of anil hydrolysis or transimination. The above observations together with detailed kinetic measurements[10] lead to the conclusion that the rate of reaction 1 is determined by the rate of attack of aniline held in the second coordination sphere of the metal complex on acetone coordinated to the metal ion and that of reaction 2 by the rate of attack of second-sphere aniline on complexed anil.

There remains an interesting question as to how the isomerization process d is related to the other reactions. Clearly, reaction 1 will bring about exchange of the cis and trans methyl groups so (d) must be at least as fast as (a). Reaction 2 may or may not bring about isomerization, depending on whether there is a stereospecific attack of aniline on anil or an intermediate exists containing a single bond between carbon and nitrogen, e.g., a carbinolimine. On the other hand, catalyzed isomerization of the anil could be a distinct process faster than either reaction 1 or reaction 2 involving rotation about the C–N bond of complexed anil. In this case the rate will be independent of aniline concentration. If this is the case, the rate parameters for isomerization will provide some information

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on the extent of polarization of the C=N bond brought about by metal complexation and hence on the importance of this polarization in activating the anil for nucleophilic attack, i.e.
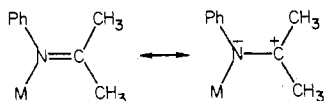
The only previous information on this topic was a single experiment which leads to an ambiguous result.[9] It was found that the rate of ^{19}F exchange between *p*-fluoroaniline and its acetone anil (in the presence of catalyst) was approximately twice the rate of exchange of the anil methyl groups. This leads to the tentative conclusion that isomerization occurred only during the transimination reaction with an equal probability of methyl-group exchange or of retaining the original configuration. It was recognized, though, that the numerical agreement of the rates might be fortuitous and that a more extensive investigation of the point was merited. We report some pertinent experiments below.

Spin-Saturation-Transfer Experiments

Nuclear magnetic resonance may be used in three distinct ways to obtain information on chemical rate processes. If a reaction is relatively slow, the spectrum may be repetitively scanned and the rate of decrease of a reactant peak or of increase of a product peak measured. Catalyzed anil formation or hydrolysis may be studied in this manner. Rapid-exchange reactions may lead to broadening or coalescence of NMR peaks. This effect has been extensively used in kinetic studies. There are some reactions which are too rapid to be conveniently followed by repetitive scanning but not sufficiently rapid to lead to line-broadening effects. Such reactions can be conveniently studied by spin-saturation-transfer experiments.[11,12] The necessary condition is that T_1, the spin-lattice relaxation time, should be similar in magnitude to τ, the lifetime for the exchange process. Catalyzed isomerizations of anils proceed at a suitable rate for this technique.

Forsen and Hoffman[11,12] considered the time dependence of the magnetization of two chemically exchanging spins during irradiation of one of them. The intensity of one signal A, upon the saturation of other signal B, follows a first-order decay described by the expression

$$M_z^A(t) = M_0^A [(\tau_1^A/\tau^A) \exp(-\tau/\tau_1^A) + (\tau_1^A/T_1^A)] \quad (3)$$

M_z^A is the magnetization in the z direction, and M_0^A is the value of M_z^A in the absence of irradiation at B. τ_1^A is defined

$$1/\tau_1^A = 1/\tau^A + 1/T_1^A \quad (4)$$

where τ^A is the average lifetime of the spin at site A and T_1^A is the spin-lattice relaxation time of the nucleus A. After continued irradiation at site B, the equilibrium intensity of A will be

$$M_z^A(\infty) = M_0^A \tau_1^A/T_1^A \quad (5)$$

We may define a factor R such that

$$R^A = M_z^A(\infty)/M_0^A = \frac{\tau_1^A}{T_1^A}$$

From eq 4

$$1/\tau^A = ((1/R^A) - 1)/T_1^A$$

A knowledge of T_1^A and R^A suffices to determine τ^A. τ_1^A (hence T_1^A) may be determined by observing the decay of M_z^A

on applying the saturating field at B (eq 3). It is however generally more convenient to measure R^A and determine T_1^A in a separate experiment.

Conventionally, T_1 is determined by saturation-recovery or inversion-recovery pulse techniques. Such experiments are inappropriate for an exchanging system with a lifetime comparable to T_1, because the recovery of magnetization is a composite function of various time constants.[11] Indeed, it has been experimentally observed that the "apparent" T_1's are dependent upon the amount of catalyst added for these anil isopropylidine methyl groups. However, when the exchange rate is significantly slower than spin-lattice relaxation, the above schemes yield good approximations to T_1.

T_1 may therefore be determined by conventional methods in the absence of catalyst. Since the concentration of catalyst ($\sim 10^{-3}$ M) is much less than the concentration of anil (~ 0.5 M), it is reasonable to assume that these diamagnetic catalysts do not directly affect T_1.

If, however, other time-dependent processes in addition to spin saturation transfer are present, the observed quantity $(1/R - 1)/T_1$ may not yield true exchange rates. Specifically nuclear Overhausser effects[13] can interfere but they may be easily recognized (see below). In the absence of such effects R and T_1 provide a measure of the exchange rate.

Experimental Section

Preparation of Chemicals. $Zn(tu)_4(ClO_4)_2$ was prepared by warming a stoichiometric mixture of zinc perchlorate hydrate and thiourea in enough 2-propanol to bring about complete dissolution. The solution, after boiling for 10 min, was filtered and cooled at 0 °C for at least 30 min. Chloroform was added until turbidity persisted. Crystallization may be initiated by scratching. Recrystallization was performed by repeating the above procedure.

All anils were prepared by equilibrating 10 g of the appropriate aniline in 40 mL of acetone over 10 g of molecular sieve at subzero temperatures for several hours, with the molecular sieve changed at least once. Proton NMR indicates 100% yield in less than 5 h. The solution was filtered, and excess acetone was removed by evaporation under vacuum. The anil thus obtained was purified by distillation under vacuum at 70–110 °C. This method resembles the one reported previously by Kyba.[14] All earlier published methods[15,16] either failed or gave a yield too low to be of practical value.

The anils successfully prepared by the above method are those of aniline, *p*-toluidine, *p*-anisidine, *p*-fluoroaniline, *p*-chloroaniline, *p*-bromoaniline, *m*-nitroaniline, and benzylamine. All except that of *m*-nitroaniline are colorless liquids at room temperatures. The *p*-anisidine anil may crystallized out by cooling to 18 °C. The *m*-nitroaniline anil is a reddish brown liquid. Anils were characterized by their NMR spectra, IR spectra, and boiling points all of which agreed with literature values. The NMR spectra in carbon tetrachloride show the *N*-isopropylidene methyl resonances at 1.6 and 2.4 ppm relative to Me$_4$Si. The infrared spectra show a strong absorption at 1670 cm^{-1}.

Acetonitrile-d_3 was dried over molecular sieve and distilled before use.

NMR. Experimentally, the spin-saturation-transfer (SST) experiments were performed on a Varian EM-390 cw spectrometer equipped with an EM-3930 homonuclear spin decoupler and an EM-3940 variable temperature accessory. Spectra were obtained without lock if possible to avoid interference with the decoupler frequency. The observing rf power was also kept below the 0.02-mG setting to avoid saturation. Spinning also modulates the decoupler frequency, and the spinning rate was adjusted to greater than 40 Hz since the signals of the exchanging spins were 33 Hz apart. The sweep width was 1 ppm so that the decoupler frequency may be set with adequate precision. It is necessary to establish optimum decoupler power settings—too low a setting leads to incomplete saturation and

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Table I. SST Results for Catalyzed Anil Isopropylidine Exchange Reactions in Acetonitrile-d_3 at 29.6 °C (Catalyst $Zn(tu)_4(ClO_4)_2$)

anil subst	10^3[Cat], M	signal A			signal B		
		T_1, s	R	$\dfrac{10(1/R-1)/}{T_1, s^{-1}}$	T_1, s	R	$\dfrac{10(1/R-1)/}{T_1, s^{-1}}$
p-CH$_3$	0	3.84	0.928	0.208	3.29	0.982	0.061
	1.37		0.362	4.58		0.550	2.49
	2.63		0.280	6.68		0.343	5.84
p-OCH$_3$	0	3.96	0.894	0.303	3.12	0.987	0.32
	0.7		0.299	5.90		0.453	3.87
aniline	0	3.67	1.0	0	3.55	0.91	0.281
	0.7		0.81	0.627		0.81	0.647
	1.37		0.61	1.74		0.61	1.8
	2.01		0.42	3.76		0.56	2.22
	2.63		0.33	5.53		0.40	4.22
p-F	0	3.16	1.19		3.34	0.94	0.18
	0.7		1.02			0.91	0.30
	2.01		0.69	1.43		0.65	1.62
	3.78		0.33	6.43		0.40	4.49
p-Cl	0	3.86	0.94	0.16	3.23	0.92	0.28
	0.7		0.79	0.70		0.80	0.77
	1.37		0.59	1.79		0.66	1.61
	2.63		0.49	2.69		0.57	2.32
	3.78		0.43	3.42		0.51	2.97
p-Br	0	3.49	0.93	0.23	2.83	0.94	0.21
	0.7		0.87	0.43		0.96	0.14
	2.01		0.77	0.86		0.80	0.88
	3.78		0.63	1.69		0.64	1.98
	8.85		0.50	2.87		0.58	2.54
m-NO$_2$	0	3.74	0.76	0.86	2.97	0.83	0.67
	0.7		0.74	0.94		0.81	0.77
	2.01		0.76	0.86		0.83	0.67
	4.33		0.76	0.86		0.84	0.64
	6.77		0.68	1.26		0.83	0.67

too high a setting leads to interference at the observing frequency. This was accomplished by comparing the observed intensities at different decoupler power settings for an exchanging and a nonexchanging system with the same chemical shift difference.

T_1's were determined by an inversion-recovery sequence on a Bruker WH-90 pulse Fourier transform NMR spectrometer with quadrature detection. Such determinations were performed on uncatalyzed anil samples. Some SST experiments were also performed on this instrument in cases where the exchanging signals had a small chemical shift separation, e.g., the p-methyls of toluidine and its anil and the p-methoxy of the p-anisidine system.

Results

(a) Uncatalyzed Isomerization. It has been reported that isomerization leads to the coalescence of the two NMR methyl peaks of N-isopropylideneaniline at 140 °C in quinoline[17] and at 126 °C in diphenyl ether.[18]   For the latter solvent an activation energy of 22.3 ± 2.0 kcal/mol was reported. Solutions in acetonitrile-d_3 show no spin-saturation-transfer effect at room temperature, but the effect becomes apparent above 30 °C. The temperature dependence of the spin-saturation-transfer effect was measured over the range 30–70 °C to determine whether rates measured by this technique are consistent with those obtained by the more usual line-broadening method at higher temperatures.

Figure 1 shows a plot of the parameter log $(1/R - 1)$ vs. $1/T$ for the two methyl signals of N-isopropylideneaniline. These measurements were carried out by using a solution in acetonitrile-d_3 containing about 10% benzene by volume to provide a lock signal. The points for the two signals fall on parallel lines—since $(1/R - 1)$ corresponds to T_1/τ, this indicates that the T_1's for the two resonances are slightly different. Both T_1 and τ are temperature dependent. The temperature dependence of T_1 will be reflected in the temperature dependence of the viscosity. That of τ is determined by the
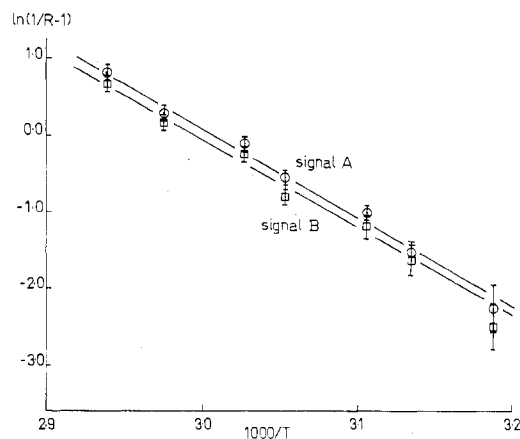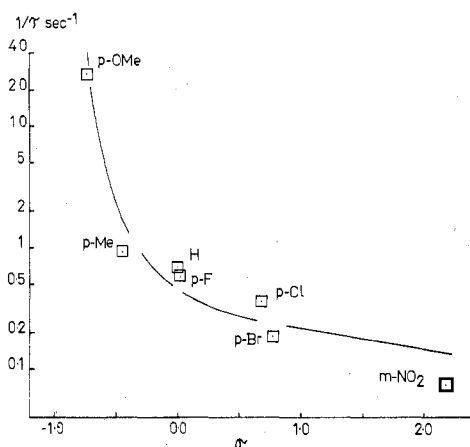
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Figure 1. Temperature dependence of rate of isopropylidene methyl exchange for the acetone anil of aniline, in acetonitrile-d_3 (uncatalyzed; $E_A = 21 \pm 2$ kcal).

activation energy of the isomerization process. We estimate a correction of 1.65 kcal/mol for the temperature dependence of the viscosity which, combined with the measured slope of Figure 1, gives a value of 21 ± 2 kcal for the activation energy for isomerization. This is in satisfactory agreement with the value of 22.3 ± 2.0 kcal quoted above. Similar experiments on the m-nitroaniline anil gave an identical activation energy of 21 ± 2 kcal.

(b) Catalyzed Isomerization. The catalyzed isopropylidine exchange of the anils in acetonitrile-d_3 was studied by monitoring the SST intensities of the NMR signals of the methyl protons. Solutions 0.67 M in anil were used, and the concentrations of catalyst $Zn(tu)_4(ClO_4)_2$ were varied. The values of R and T_1 are listed in Table I. The final column gives $1/\tau^A$ ($\equiv (1/R - 1)/T_1$), the rate of methyl-group exchange. Agreement between the values obtained for the two signals is moderately good in most cases, and the rates are generally proportional to catalyst concentration. Deviation from linearity

Figure 2. Variation of methyl exchange rate with aromatic substituent. Constant catalyst concentration $[Zn(tu)_4(ClO_4)_2] = 4 \times 10^{-3}$ M (σ from pK_a's of substituted anilines).

is observed for two systems at low exchange rates, namely, the aniline anil and the p-fluoroaniline anil. The latter is an obvious example of the interference of SST by the nuclear Overhausser effect; the intensity of A is actually enhanced, rather than diminished, at low catalyst concentration when B is irradiated and vice versa. At higher catalyst concentrations and exchange rates, the SST effect dominates, and the exchange has a decoupling effect, thus eliminating the NOE and allowing exchange rates to be obtained.

It is clear from the results in Table I that if the aniline bears an electron-donating substitutent such as OCH_3 there is a strong catalytic effect but that for electron-withdrawing substituents such as NO_2 the effect is small or negligible. Figure 2 shows a plot of rate vs. Hammett σ. The temperature dependence of the exchange process for the aniline anil has been measured in the presence of 6×10^{-3} M zinc thiourea perchlorate as a catalyst. The measurements yield an activation enery of 13 ± 2 kcal, i.e., about 8 kcal less than for the uncatalyzed reaction.

(c) Transimination Reactions. The transimination reaction (eq 2) can occur if both anil and aniline are present in solution at the same time. If there is a suitable substituent on the phenyl ring, catalyzed transimination can be studied by spin-saturation-transfer experiments and the rate compared with that for isopropylidine methyl exchange. Addition of a little water to a solution of an anil will produce the corresponding aniline by hydrolysis. Such a mixture is suitable for investigating transimination.

The p-fluoroaniline anil system has been studied in this manner.[9] An experiment in the presence of catalyst in which the rate of exchange of the p-F substituent between aniline and anil was compared with the rate of exchange of the isopropylidene methyl groups gave $\tau(CH_3)$ as 1.55 (s) and $\tau(F)$ as 0.72 (s). This result is consistent with the notion that exchange of the methyl groups results from the same rate process as transimination with there being an equal probability of transimination leading to retention or exchange of the methyl-group positions. We have extended these experiments by examining the systems comprising p-anisidine and p-toluidine together with their acetone anils. In each case transimination can be followed by SST experiments involving the methyl groups attached to the aromatic rings and isomerization can be examined with use of the same solutions. The results are presented in Table II. The ratio $\tau(\text{anil})/\tau(\text{aniline})$ should be equal to the ratio of the concentrations [anil]/ [aniline]. The agreement of these ratios is good in both cases. In the absence of catalyst no SST is observed at 25 °C. In the presence of catalyst the rate of methyl-group exchange is greater than that of transimination in both cases. For p-

solution: p-anisidine anil + D_2O + p-anisidine + acetone
[anil] + [aniline] = 0.227 M
$[Zn(tu)_4(ClO_4)_2] = 1.66 \times 10^{-3}$ M
[anil] / {[anil] + [aniline]} = 0.667

	anil		aniline
	O-Me	isopropylidine	O-Me
T_1, s	3.75	3.76	3.43
R	0.384	0.279	0.267
$1/\tau$, s^{-1}	0.428	0.678	0.800

[anil]/[aniline] = 2.0
$\tau(\text{anil})/\tau(\text{aniline})(\text{OMe}) = 1.9$

solution: p-toluidine anil + D_2O + p-toluidine + acetone
[anil] + [aniline] = 0.26 M
$[Zu(tu)_4(ClO_4)_2] = 1.37 \times 10^{-4}$ M
[anil] / {[anil] + [aniline]} = 0.685

	anil		aniline
	$PhCH_3$	isopropylidine	$PhCH_3$
T_1, s	6.71	7.80	10.7
R	0.89	0.332	0.71
$1/\tau$, s^{-1}	0.018	0.26	0.038

[anil]/[aniline] = 1.9
$\tau(\text{anil})/\tau(\text{aniline})(\text{CH}_3) = 2.1$
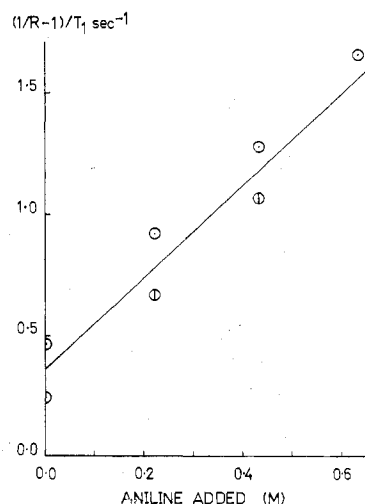
Figure 3. Variation of rate of isopropylidene methyl exchange with aniline concentration. $T = 29.6$ °C and catalyst $[Zn(tu)_4(ClO_4)_2] = 2.01 \times 10^{-3}$ M. The two sets of points are from independent experiments involving irradiation of the two different methyl groups.

anisidine anil the difference is $\sim$50%, and for the p-toluidine it is a factor of 10. Clearly the case of p-fluoroaniline for which methyl-group exchange was half as fast as transimination is not representative.

The question remains as to whether the transimination reaction is contributing to the rate of isomerization or whether the latter process is quite independent of the former. This point was investigated by examining the dependence of the rate of isomerization on aniline concentration. Some results are shown in Figure 3. In this figure the rate parameter for methyl-group exchange is plotted against the concentration of aniline added to anil solution. The rate is clearly proportional to aniline concentration, as required by the transimination mechanism, but there is a significant intercept at zero aniline concentration, indicating a contribution from another mechanism. The nature of this alternative mechanism will be discussed below.

Discussion

The mechanism of the uncatalyzed isomerization of anils

has been discussed extensively. Kalinowski and Kessler[19] have reviewed the subject. Three major mechanisms have been considered: (a) polarization of C=N to C^+—N^- followed by rotation about the C—N bond, (b) inversion about the nitrogen giving a linear C=N—C transition state, and (c) the formation of an intermediate carbonyl amine. The last mechanism can be directly eliminated for the present catalyzed reactions by the observation that exchange of CH_3 with CD_3 is much faster than exchange with CH_2D. For the uncatalyzed reaction, the weight of the evidence favors the nitrogen inversion mechanism[19] b. Among the evidence quoted in support of this conclusion is the observation that formation of a complex between the imine and aluminum trimethyl completely inhibits isomerization.[20] The rate of the uncatalyzed reaction is increased by electron-withdrawing substituents on the nitrogen. That of catalyzed reaction is dramatically increased by electron-donating substituents on the nitrogen. Clearly a different mechanism is involved. Complexation to the metal ion is strongly suggested. Electron-donor substituents will increase the Lewis basicity of the imine nitrogen and favor complexation to a metal ion. Such complexation will prevent inversion but will favor C—N rotation by polarization of the bond. A rotation mechanism is therefore indicated for the catalyzed process.

Complexation to a metal ion will clearly reduce the C=N bond order and facilitate rotation. Attack by a nucleophile to give a carbinolimine type of intermediate will accomplish the same end, e.g.
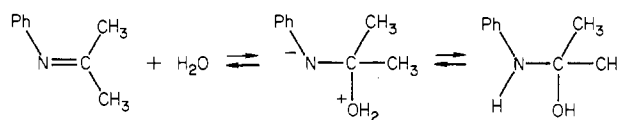
The most reasonable interpretation of the above results would seem to be that both metal complexation and nucleophilic attack are necessary to bring about isomerization. The term in the rate equation proportional to aniline concentration represents the effect of aniline as a nucleophile, i.e., transimination. The term independent of aniline could well represent the contribution of other nucleophiles, i.e., solvent (acetonitrile), water, anil, and thiourea, present in the solution.

This interpretation is consistent with our previous mechanistic conclusions concerning anil hydrolysis and transimination. The rate-determining step in these reactions is the rate of attack of a nucleophile (water or aniline) held in the second coordination sphere of the catalytic complex on anil coordinated to the metal ion. The rate of isomerization is greater than either anil hydrolysis or transimination because it is determined by the sum of the rates for all the nucleophiles present including probably solvent molecules which cannot react with the anil to give a new product.

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Structure and Bonding in Chloro- and Bromobismuthate(III) Clusters (BiX₄⁻, Bi₂X₉³⁻, BiX₆³⁻) by NQR Spectroscopy

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The structural aspects of difficultly characterized halobismuthate(III) salts have been probed by using chlorine and bromine NQR spectroscopy. The presence of bridging and terminal halogen atoms is clearly evident in BiX_4^- and $Bi_2X_9^{3-}$ salts, X = Cl, Br. Some BiX_6^{3-} salts contain discrete regular octahedral anions while others show evidence of bridging, or at least strongly associated, halogen atoms. The Raman spectra of these salts yield less decisive structural information than do the NQR spectra. General trends in ionicity as a function of the net charge on the structural unit are apparent in the NQR data now available for $BiBr_2^+$, $BiBr_3$, $BiBr_4^-$, and $BiBr_6^{3-}$ and $BiCl_3$, $BiCl_4^-$, and $BiCl_6^{3-}$. The bonding trend in $M_2X_9^{3-}$, M = Tl, Sb, Bi, is dominated by the effect of the ns^2 electron pair in the Sb and Bi.

Introduction

Bismuth(III) halide salts, through clustering of the anions, crystallize in a wide range of subtly complex structures. Salts having ion stoichiometries of $BiBr_2^+$,[1] BiX_4^-,[2,3] BiX_5^{2-},[4,5] BiX_6^{3-},[2,3] BiX_7^{4-},[2,3] $BiCl_9^{6-}$,[2] $Bi_2Br_8^{2-}$,[6] $Bi_2X_9^{3-}$,[4,7] $Bi_2X_{10}^{4-}$,[4,6] $Bi_2Cl_{11}^{5-}$,[2] $Bi_3Cl_{14}^{5-}$,[2] and $Bi_3Cl_{16}^{7-}$[8] where X = Cl⁻, Br⁻ have

been claimed, but not all have been studied with the same degree of rigor. The stoichiometry obtained appears to depend upon the cation, the concentration of the species in the crystallizing medium, and the solvent.[9] Some of the complexes may be double salts or mixtures. This occurrence has been noted in similar antimony halide systems where, for example in $Sb_2Br_{11}^{5-}$, the $Sb_2Br_9^{3-}$ ion and two Br⁻ ions cocrystallize in the lattice.[10]

A systematic study directed at classifying the interactions in these systems has not appeared, probably in part because

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