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Oligomerization of Trichloroacetonitrile (TCA) by Metal Salts

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A $C \equiv N$ bond was found to transform into a $C=N$ bond under such a mild conditions as to mix trichloroacetonitrile, metal salts and methanol at 20 C. Ni(II) and Co(II) gave dimeric ring complexes and Mn(II) gave amidine, aminotriazine and brown powder. The aminotriazine was isolated as unstable liquid which spontaneously transformed into the crystal. A trimer structure was proposed for the liquid. In anhydrous systems, any oligomerization did not occur, so water was concluded to participate in the initiation.

Keywords——trichloroacetonitrile; metal salt; methanol; nitrile; imino bond; dimeric ring complex; amidine; aminotriazine; trimer

Polymers containing $C=N$ double bonds in the main chain have been attracting greater attention due to their valuable properties, particularly semiconducting and dielectric properties. A number of investigators have persevered with their efforts for producing the polymers. Recently, Suematsu and co-workers[1] reported a new method for the syntheses of various non-conjugated polyimines and described their electrophysical properties. However, the polymers consisting of only conjugated $C=N$ bonds have not been successfully synthesized till recently. They are typically prepared by nitrile-polymerization. Kabanov and co-workers[2] obtained black powders having $C=N$ absorptions on the infrared spectra, by heating the complexes of some nitriles and Lewis acids such as $TiCl_4$ and $ZnCl_2$. Tabata and co-workers[3] reported the partial synthesis of $\leftarrow\!\!RC=N\!\!\rightarrow_n$ (where R is an alkyl or aryl moiety and n the degree of polymerization), which were produced as by-products of gamma ray polymerization of methacrylonitrile. Jones[4] obtained the polymer by the homopolymerization of perfluoroalkylnitrile under high pressure of 7000 to 20000 kg/cm^2. Peeble and co-workers[5] prepared that by the polymerization of succinonitrile using a base for initiation. However, most conjugated $\leftarrow\!\!RC=N\!\!\rightarrow_n$ reported in various articles were structurally complicated, making their characterization impossible. In this paper, a new nitrile-oligomerization under mild conditions using metal salts and the identification of the products, are described.

Experimental

The identification of products was confirmed by molecular weight determination (electron impact-mass spectrum (EI-MS)), elemental analyses, infrared (IR) spectroscopy (Hitachi model 285) and nuclear magnetic resonance (NMR) spectroscopy (JEOL PS-100). All the reactions were carried out in methanol at 20°C using a conventional apparatus with a mechanical stirrer. Typical procedures are described below.

Reaction of Trichloroacetonitrile (TCA) with $NiCl_2$——0.5 g (2.1 mmol) of $NiCl_2 \cdot 6H_2O$ was dissolved in a mixture of 20 ml of anhydrous methanol and 0.13 ml of H_2O. To the mixture was added 4.38 g (30 mmol) of TCA and stirred for 48 h at 20°C. The resultant red solution was evaporated to give orange solid. Recrystallization from xylene gave red crystals (IV) (0.5 g; 36%). mp 205.5°C. *Anal.* Calcd for $C_8H_4Cl_{12}N_6$ Ni: C, 14.37; H, 0.60; Cl, 63.78; N, 12.58; Ni, 8.67. Found: C, 14.18; H, 0.74; Cl, 61.85; N, 12.40; Ni, 9.14. IR ($CHCl_3$): 3340 cm^{-1} (sharp, νN–H), 1580 cm^{-1} ($\nu C=N$), 840, 815 cm^{-1} (νC–Cl). NMR ($CDCl_3$) δ: 6.0 (br s). UV $\lambda_{max}^{CHCl_3}$ (nm) 255 ($\varepsilon = 1.9 \times 10^4$), 305 ($\varepsilon = 5.6 \times 10^3$), 350 ($\varepsilon=2.1\times10^3$), 370 ($\varepsilon=2.1\times10^3$). MS *m/e*: 662 ($M^+$).

Reaction of TCA with Mn (II) Salt——0.85 g of anhydrous Mn $(OCOCH_3)_2$ and 5 ml of TCA were dissolved in 20 ml of anhydrous methanol. The mixture was stirred for 48 h at 20 °C and evaporated in a frozen state. The residue was chromatographed on a silica gel using CCl_4 as eluent. 2.91 g of colorless liquid (I) was obtained (33%). IR (liquid): 3350 cm^{-1} (sharp, νN–H), 1670 cm^{-1} (νC=N). ^{1}H-NMR ($CDCl_3$) δ: 8.45 (br s, NH), 4.01 (3H, s, OCH_3). ^{13}C-NMR ($CDCl_3$) δ: 56.3 (OCH_3), 91.0 (CCl_3), 163.0 (C=NH). MS *m/e*: 176 (MH^+).

The same experiment was carried out in the presence of water to determine whether oligomeric material was formed, and yielded 49% of II, 8.5% of a viscous liquid and 43% of brown powder (Run 7 in Table I). The viscous liquid which was unstable, showed a single νC=N (1650 cm^{-1}), νNH or NH_2 (3470, 3325 cm^{-1}) and νCCl (810, 760 cm^{-1}) absorptions on the infrared spectrum. But, on standing at room temperature, it turned spontaneously into the crystal (III).

II: mp 195 °C. IR (KBr): 3250, 3200 cm^{-1} (νNH_2), 1660 cm^{-1} (νC=N), 840, 820 cm^{-1} (νC–Cl). MS *m/e*: 160 (M^+), 117 (CCl_3).

III: mp 71 °C (dec.). IR (KBr): 3500, 3350 cm^{-1} (νNH_2), 1680, 1665, 1650 cm^{-1} (νC=N), 840 cm^{-1} (νC–Cl). ^{1}H-NMR ($CDCl_3$) δ: 6.5 (br s, NH_2). MS *m/e*: 328 (M^+), 293 ($[M-Cl]^+$).

Brown Powder: IR (KBr): 3345 cm^{-1} (νNH), 1570 cm^{-1} (νC=N), 820, 680 cm^{-1} (νC–Cl).

Results and Discussion

Trichloroacetonitrile (TCA) smoothly reacted with metal salts to give oligoimines. The results are summarized in Table I. Ni(II) salts produced red crystals in good yields. It was identified as (IV) (Chart 1) on the basis of the MS (typical isotope peaks characteristic of the compound having twelve Cl and one Ni atoms: see Table II), IR (a sharp and single peak of NH at 3340 cm^{-1} and an intense peak of conjugated C=N at 1580 cm^{-1}), NMR and elemental analyses. Co(II) also gave a similar product (Run 5). However, under anhydrous conditions no reaction occurred, indicating the participation of H_2O in initiation (Run 4).

Mn(II) gave quite different products. An anhydrous system produced only an adduct (I) in good yield (Run 6). However, the addition of H_2O produced an amidine (II), an

Table I. Oligomerization of TCA in Methanol by Metal Salts

Run	Metal salt concentration (mmol)		TCA concentration (mmol)	Added H_2O (mmol)	Reaction time (h)	Products yield (%)			
						I	II	III	IV
1	$NiCl_2$	2.1	30	20	48	0	0	0	36
2	$Ni(OH)_2$	2.1	30	20	168	0	0	0	2
3	$Ni(OCOCH_3)_2$	4.4	132	40	48	0	0	0	76
4	$Ni(OCOCH_3)_2$	4.4	132	0	48	0	0	0	0
5	$Co(OCOCH_3)_2$	1.0	20	10	72	0	0	0	35
6	$Mn(OCOCH_3)_2$	5.0	50	0	48	33	0	0	0
7[a]	$Mn(OCOCH_3)_2$	10.0	70	50	48	0	49	8.5	0
8	$Mn(OCOCH_3)_2$	0.6	30	0.5	48	26	8	0	0

The yields of I—III are based on TCA and that of IV on the metal salt.
a) Brown powder was obtained in 43% yield.

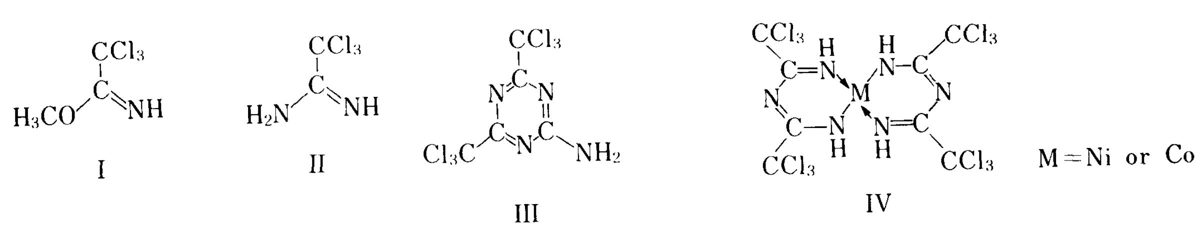
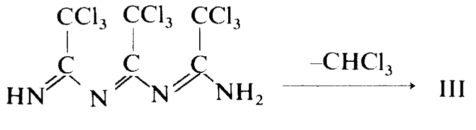


Chart 1

Table II. Isotope Peaks in Mass Spectra

Compound	Molecular mass		Relative intensity	
			Calcd	Found
II	$[M]^+$			
	160		100.0	100.0
	162		97.5	97.3
	164		31.7	32.8
	166		3.4	8.9
III	$[M-1]^+$	$([M]^+)$		
	327	(328)	51.2	51.0 (50.9)
	329	(330)	100.0	100.0 (100.0)
	331	(332)	81.2	79.3 (78.9)
	333	(334)	35.2	32.0 (43.9)
	335	(336)	8.5	8.8 (14.0)
	337	(338)	1.1	1.3 (—)
IV	$[M]^+$			
M=Ni	662		9.6	10.3
	664		41.3	43.3
	666		81.7	84.5
	668		100.0	100.0
	670		84.6	85.6
	672		51.9	52.6
	674		25.0	23.7

aminotriazine (III) and a considerable amount of a brown powder (Run 7 and 8). The structural determinations were based on IR, NMR and MS analyses (the isotope peak analyses are shown in Table II). We know of no previous report concerning imino bond formation from nitrile under such mild conditions as these. The compound (III) was isolated initially as an unstable, viscous liquid which exhibited a quite different infrared spectrum. On standing at room temperature, the liquid transformed spontaneously and quantitatively into the crystal (III). Although the mechanism and the product analyses have not been studied in detail, the liquid may be presumably a linear trimer represented by the formula (V), which may transform into III with the elimination of one molecule of chloroform according to Eq. (1).



V

(1)

The source of the NH moiety of the products (II), (III) and (IV) may be the result of catalytic hydrolysis of TCA. But, it is apparent that the oligomerizations did not involve the formation of free amine followed by substitution for chlorine or others, for the addition of ammonia or *n*-butylamine to the anhydrous systems was found not to result in the formation of (II), (III) or (IV). Therefore, it seems probable that the metal salts combine with the nitrile to produce π-bonded complexes followed by metal-catalyzed hydrolysis and oligomerization. In fact, a strong ligand-containing metal salt such as $Cl_2Ni\ (PPh_3)_2$ was inactive, hindering the co-ordination of TCA. The detailed reaction mechanism is currently under investigation in our laboratories.

Unlike Ni(II) and Co(II), Mn(II) did not gave the ring complex. This result can easily be ascribed to the difference of ligand field stabilization energy (LFSE). Ni(II) and Co(II) have 7 and 6 electrons respectively, in their 3d orbitals, resulting in positive LFSE. On the other hand, Mn(II) has 5 electrons, thus the LFSE is zero, which makes the ring complex formation disadvantageous.

The brown powder obtained in Run 7 was structurally complicated containing some intractable impurities. This hesitated us to purify the product. It seems, however, that there is a considerable amount of high molecular weight $\text{-}(\text{RC}=\text{N})_n\text{-}$, on the basis of the infrared spectroscopy. It exhibited a sharp, strong absorption at 1570 cm^{-1} characteristic of the conjugated C=N bond, with CCl_3 (820, 680 cm^{-1}) and NH (3345 cm^{-1}) absorptions.

In conclusion, TCA was transformed into dimeric co-ordination complexes with Ni(II) and Co(II) salts, and into linear oligomers $\text{H}_2\text{N}\text{-}(\text{RC}=\text{N})_n\text{-}\text{H}$ with Mn(II) salt, although the trimer turned easily into the aminotriazine structure.

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