REACTION OF ALUMINIUM BROMIDE WITH NITROMETHANE

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Aluminium bromide reacts in solution with nitromethane at room temperature. The reaction exhibits an induction period (about 70 hours for 0·8M solution); thereafter, however, a fast gelation of the solution occurs. Of the reaction products the following were identified: bromonitromethane, carbon monoxide, hydroxylamine hydrobromide, cyanamide dihydrobromide. Aluminium bromide is transformed in the reaction to $Al(Br)_{3-x}(OH)_x$.

It has been known that aluminium bromide and nitromethane form a 1 : 1 molecular complex containing a dative bond between aluminium and oxygen of the NO_2 group. This complex can be isolated as a solid substance and decomposes[1] only at 85°C. No other reaction, besides that one of the formation of the complex, was observed when electrical conductivity of the $AlBr_3$ and CH_3NO_2 solutions was measured[2]. However, we observed that solutions of $AlBr_3$ in nitromethane were not stable; their ability to oxidize aromatic hydrocarbons to radical cations decreased gradually and gelation occurred after a longer time in solutions 0·5M or more concentrated. As nitromethane serves also as a solvent in cationic polymerization studies, we undertook a closer investigation of reactions taking place between the primarily formed complex $AlBr_3 . CH_3NO_2$ and nitromethane. Also, we attempted identification of some of the products formed during the interaction of both components.

EXPERIMENTAL

Chemicals. Aluminium bromide was prepared by the reaction of both constituent elements in nitrogen atmosphere, and was purified by vacuum destillation. Nitromethane (Xenon, Lodž) was fractionated on a distillation column; shortly before use it was heated under a reflux condenser with CaH_2 for about 4 hours and then redistilled.

Preparation of solutions. Nitromethane was carefully degassed *in vacuo* and then distilled into the mixing vessel with five ampules. After cooling down by liquid nitrogen, $AlBr_3$ was distilled to it. The mixing vessel was then sealed off from the vacuum line and the mixture was melted. The clear solution was distributed into the side ampules (usually provided with two breakable seals)

and the ampules were then sealed off, too. Each ampule contained 25 ml of 0·8M solution of $AlBr_3$ which was left to react at room temperature, until gel was formed from the solution.

Product analysis. Isolated products were investigated by elemental analysis, and with the use of infrared spectroscopy and mass spectrometry. Solid samples for infrared spectra studies were prepared by the nujol technique in nitrogen atmosphere. Solid samples for mass spectrometric analysis were placed into capillaries under argon atmosphere and then evaporated in a direct inlet system straightly into the ionization chamber kept at a temperature about 10°C higher then the capillary. The machine used was a MCH 1303 mass spectrometer with the maximum temperature of sample evaporation 230°C. Gaseous products, sealed in ampules with breakable seals were determined with the use of a MCH 1302 mass spectrometer at reservoir pressures about 1 Torr.

RESULTS

The reaction between $AlBr_3.CH_3NO_2$ and CH_3NO_2 was investigated in detail at room temperature over the concentration range 0·5—0·8M. The reaction exhibits an induction period: during three days the viscosity of the solutions did not change, only a change in colour (to yellowish) was observed. After 4—5 days the solutions turned to yellowish gels. The rate of the reaction was not influenced by daylight.

Isolation and Identification of Products

Carbon monoxide. Solid reaction mixture (25 ml of 0·8M solution of $AlBr_3$ in CH_3NO_2) was cooled by liquid nitrogen and the gaseous portion above the frozen mixture was identified by means of the mass spectrometer as carbon monoxide. After heating the samples to dry ice temperature its total amount was determined by the volumetric method. In the ampule containing 20 mmol of $AlBr_3$, 3—4 mmol of CO were detected.

Bromonitromethane. From the same sample, thereafter, all the volatile substances were evaporated at room temperature and a pressure about 10^{-4} Torr. The distillate was trapped in a flask at liquid nitrogen temperature; at the normal pressure then 19 ml of CH_3NO_2 was distilled away from this portion, followed by 2 ml of CH_3BrNO_2 at a reduced pressure. A residue, less than 0·1 g of a non-identified brown substance was left in the distilling flask. Bromonitromethane was identified by comparing the infrared spectrum of the isolated product with the catalogue spectrum of bromonitromethane[3].

Hydroxylamine hydrobromide. In the distillation product obtained from another ampule by the above mentioned procedure, about 0·1 g of colourless crystals crystallized after several days at 0°C. Mass spectrometric analysis and comparison of infrared spectra of the sample with those of an authentic sample proved that the crystalline substance is $NH_2OH.HBr$.

Cyanamide dihydrobromide $(NH_2=C=NH_2)^{2+} 2 Br^-$. After evaporation of volatile substances at 10^{-4} Torr the original gel broke into yellowish mass of glassy character. However, the surface of the solid residue was covered by a white crust which differed in appearance as well as in chemical composition from the glassy substance. Its mass spectrum and elemental analysis indicated it could be cyanamide dihydrobromide. Its infrared spectrum agreed with both the infrared spectrum of the sample of cyanamide dihydrobromide prepared in the laboratory and with published data[4]. An Al-containing impurity (about 0·8% by weight) found by the elemental analysis did show itself neither in the mass spectrum nor in the infrared spectrum. Cyanamide dihydrobromide was brought to the gel surface together with the volatile substances diffusing from the gel during the evaporation process.

Glassy residue. The infrared spectrum of the glassy substance (after the white crust was removed) is shown in Fig. 1. Absorption bands at 1 680 and 1 078 cm^{-1} indicate that the residue contains cyanamide dihydrobromide as a substantial admixture. Strong absorption bands at 1 630 cm^{-1} and 1 700 cm^{-1} together with a series of weak bands between 900—1 300 cm^{-1}, as well as the elemental analysis (9% Al; 52·9% Br; 10·5% N; 8·5% C; 2·9% H; 16·3% O) suggests the presence of other organic components. A broad band at 550—700 cm^{-1} together with an absorption over the region 3 200—3 400 cm^{-1} undoubtedly belongs to Al—O—H bonds and indicates a partial conversion of aluminium bromide to aluminium hydroxide bromide Al(Br)$_{3-x}$(OH)$_x$. When introducing the sample into the mass spectrometer, no different significant peaks were observed at inlet temperatures up to 230°C than those found in cyanamide dihydrobromide; the sample evaporated only partly. Heating above 100°C *in vacuo* for one hour lead to the evolution of HBr, Br$_2$, and of other non-identified substances. The infrared spectrum of the pyrolytic residue (Fig. 1) then lacked the bands in the region 900—1 300 cm^{-1} as well as the bands at 1 680 and 1 700 cm^{-1}. This shows that cyanamide dihydrobromide and other organic substances were removed by the process. A decrease of the 3 400 cm^{-1} band intensity demonstrated a partial conversion of hydroxidobromide to oxidobromide. The glassy residue was soluble in methanol; dissolving in water was accompanied by gas evolution. This gas was composed of larger amount of CO$_2$ and a smaller amount of HCN, as it was found by the mass spectrometric and chemical analysis. Precursors of both these gases are not known; however, the infrared spectrum of the glassy substance did not show any evidence of the characteristic vibration of the C≡N bond.

Mechanism of the Decomposition Reactions

The results reported here demonstrate that in solutions of AlBr$_3$ in CH$_3$NO$_2$ not only the molecular complex is formed, but that both substances react in a series of parallel and mutually dependent reactions. In the reacting system bromination of nitromethane occurs, nitromethane decomposes to NH$_2$OH.HBr and CO, presumably dehydration of nitromethane takes place with the intermediate formation of fulminic acid (C=NOH) which — after condensation with hydroxylamine and subsequent reduction — would give cyanamide dihydrobromide. The intermediate function of fulminic acid is highly probable, as nitromethane easily loses water and
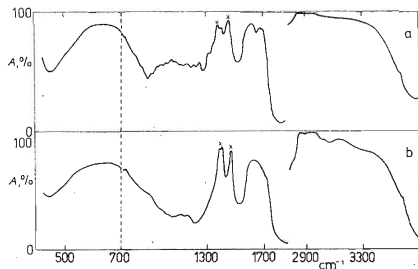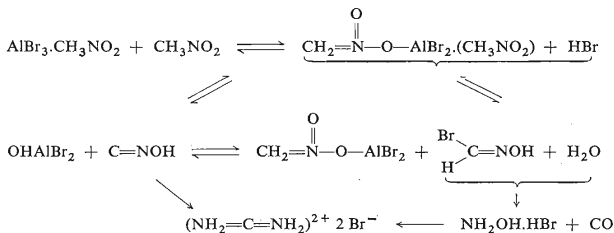

Fig. 1

Infrared Spectra of the Glassy Substance After All Volatile Substances Removal

a Gel after evaporation at room temperature and 10^{-4} Torr; b same substance evacuated for 1 hour at 100°C.

converts to fulminate[5]. Fulminates then easily add hydrogen chloride to form formylchloridoxim $H(Cl)C=NOH$ which in the presence of water decomposes to hydroxylamine hydrochloride and CO (see[6]). Furthermore, fulminates can be added in the presence of $AlCl_3$ even to, *e.g.*, benzene to form benzaldoxime or — during simultaneous water removal — benzylcyanide[5]. Thus, the addition of fulminic acid to hydroxylamine is a possible and probable way of formation of the $N=C=N$ skeleton found in cyanamide hydrobromide.

Having these facts in mind, one may suggest the following mechanism of some of the decomposition reactions of nitromethane:

$$AlBr_3.CH_3NO_2 + CH_3NO_2 \rightleftharpoons \underbrace{CH_2=\overset{\overset{O}{\|}}{N}-O-AlBr_2.(CH_3NO_2)} + HBr$$

$$OHAlBr_2 + C=NOH \rightleftharpoons CH_2=\overset{\overset{O}{\|}}{N}-O-AlBr_2 + \underset{H}{\overset{Br}{\diagup}}C=NOH + H_2O$$

$$(NH_2=C=NH_2)^{2+} 2\,Br^- \longleftarrow NH_2OH.HBr + CO$$

The decisive factor which initiates the decomposition of nitromethane by aluminium bromide is the ability of nitromethane to oxidize bromide ions to bromine. The yellowish colour of the $AlBr_3$ solutions in nitromethane which appears after a longer time is presumably caused by released bromine which is consumed in bromination of nitromethane. However, mechanisms of bromide oxidation to bromine and of the subsequent reduction of nitromethane are not known. Oxidation property of nitromethane manifests itself also in its behaviour to other aluminium halogenides: it does not react with $AlCl_3$; however, it reacts explosively with AlI_3 and iodine is evolved in the reaction practically quantitatively.

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