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Preparation and Study of Charge Transfer Complexes of N.N.N.N-Tetra-Methyl-Para-Phenylene-Diamine (TMPD) with NG, Tetryl, RDX and HMX

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Abstract. Charge transfer complexes of NG, tetryl, RDX and HMX as electron acceptors with tetra-methyl-para-phenylene-diamine (TMPD) as electron donor were prepared and studied. When the solution of nitro-explosives in an inert solvent were added to a solution of TMPD, an intense violet colour was produced. This colour is due to the formation of TMPD cation known as Wurster radical formed from TMPD through the loss of an electron. It has been shown that one mole of each of NG, tetryl, RDX and HMX is needed to form one TMPD cation. These complexes have also been studied by ultra-violet and infrared spectroscopy.

1. Introduction

Charge transfer complexes also known as π-complexes are molecular additive compounds formed by π-electron acceptor and π-electron donor molecules. In general charge transfer complexes are very unstable due to labile physical linkages between the molecules. The stability may be affected by solvent forces, steriohindrances due to groups, etc. Charge transfer complexes are of immense value for the detection, separation and identification of explosives. It is well known that *C*-nitro compounds are strong electron acceptors forming readily charge transfer complexes. Very little work has been published as regards possible electron accepting properties of $O\text{-}NO_2$ and $N\text{-}NO_2$ explosives and about the nature of such complexes. The work was undertaken to prepare charge transfer complexes of NG, tetryl, RDX and HMX as electron acceptors with tetra-methyl-para-phenylene-diamine (TMPD) as electron donor.

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Mulliken[1] studied the formation of charge transfer complexes of nitro-aromatic compounds with amines and showed that these π-complexes involve hybrid structures with only dative and no bond. Tronor[2] et al. studied charge transfer complexes of *m*-dinitrobenzene with different amino benzoic acids. Urbanski[3] reported charge transfer complexes with nitrate esters as electron acceptors. It is well known that C-nitro compounds are strong electron acceptors forming readily charge transfer compounds. Nothing much has been reported as regards possible electron accepting properties of *θ*-nitro and *N*-nitro compounds. However, Urbanski[4-8] and Witanowski[9] have found that nitric esters such as *D*-mannitol hexanitrate and erythritol tetranitrate can form additive compounds with some aromatic amines. He showed that there is an interaction between nitric esters of mono, di, tri, tetra and hexahydroxylic alcohols with aromatic amines. We prepared and studied charge transfer complexes of nitroglycerine, tetryl, RDX and HMX with TMPD.

2. Experimental

1, 2-dichloroethane (solvent) was purified according to the literature.

Preparation of TMPD

p-phenylene-diamine was added gradually to stirred, ice-cooled 90% formic acid (200 c.c.) at 10-20°C. The mixture was then warmed to 65°C and 40% aquoeus formaldehyde (280 c.c.) was added during 30 minutes with stirring. Stirring was then stopped and mixture heated at 80°C on steam bath for two hours, cooled, basified with sodium hydroxide solution and extracted with ether. The combined extracts were dried with anhydrous sodium sulphate and fractionated by distillation under reduced pressure. The fraction, b.p. 150-160°C at 27 mm pressure weighing about 9 grams partly solidified, when drained gave the pale yellow TMPD m.p. 50-51°C. The material was purified by double distillation in the nitrogen atmosphere.

Nitroglycerine was extracted from dynamite, obtained from Ordnance Factory, with the help of a acetone, washed repeatedly with distilled water at 50-70°C and finally with cold water untill it was neutral to litmus. Nitroglycerine was further purified by distillation under reduced pressure of 2 mm *Hg* and by freezing crystallization. Tetryl, RDX and HMX were purified by double crystallization from solvent.

Preparation of Charge Transfer Complexes

When a solution of nitro compound of known molarity in nonpolar or low polarity solvents was added to a solution of TMPD in the same solvent, an intense voilet colour was produced first, which slowly fades and results in pale yellow solution, showing the formation of charge transfer complexes. The intense voilet is due to TMPD cation known as Wurster radical formed from TMPD through the loss of one electron to the nitro compound acting as electron acceptor. The colour of the TMPD cation is violet and gives absorption at 570 nm and 620 nm.

CE
(TETRYL)

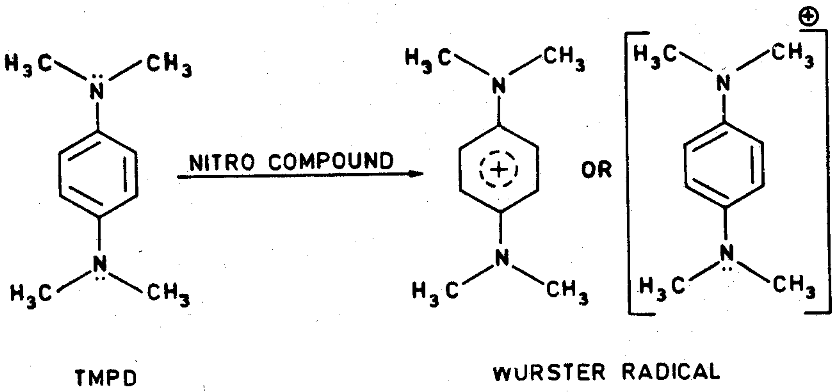

Figure 1. Formation of Wurster radical.

We have also taken electronic spectra of the Wurster radical formed by adding solutions of NG and TMPD in 1, 2-dichlorethane and obtained absorption bands at 570 and 620 nm(Fig. 1). Experiments with RDX, HMX and tetryl were also carried out which confirmed that a fast reaction of nitrate ester with TMPD in the absence of daylight leads to the formation of the bluish-violet coloured radical known as Wurster radical. The absorption bands at 570 and 620 mm are typical of Wurster radical. When the solution of nitro compound and TMPD were kept for some more time, it was observed that during next three to four hours, the absorption curve gradually changes and bands at 570 and 620 mm vanished and a new band at 450 nm characterising the yellow colour, relatively stable was obtained. This band at 450 nm is characteristic of charge transfer complex. It has been established that this change is typical of solutions in solvents with low dielectric constant such as 1, 2-dichloro-ethane, dichloro-methane and benzene. In polar solvents such as methanol, the original bluish-violet colour remained unchanged for several days and no yellow complex with band 450nm was formed.

Charge Transfer Complex of NG with TMPD

Molar solution of NG in 1, 2-dichloro-ethane was added to the molar solution of TMPD in the same solvent. An intense violet colour of 'Wurster radical' was first produced which after three hours gradually changed to yellow. The coloured charge transfer complex was studied by electronic and infra-red spectra. This coloured charge transfer complex gave absorption band at 450 nm and I.R. gave characteristic absorption peak at 1620 cm^{-1}, which is absent in the I. R. spectra of NG and TMPD. The absorption peak at 1680 cm^{-1} was due to *O-NO$_2$* which is also present in NG spectra. Another band in the complex has the frequency at 1360 cm^{-1}. The band is not present in the components i.e. NG and TMPD. It is in the region of inorganic nitrate ion (O-NO_2)$^{(-)}$. The band is assigned to *O-NO$_2$* groups in NG negativeyl charged under the influence of the electron donor TMPD of a low ionisation constant, charge transfer complex of NG-TMPD could not be isolated from the solution. Evaporating the solvent at low temperature and under reduced pressure left only brown tarry material showing signs of decomposition with evolution of nitrogen dioxide (Fig. 2). This is due to the low stability of nitrate esters in presence of basic compounds.

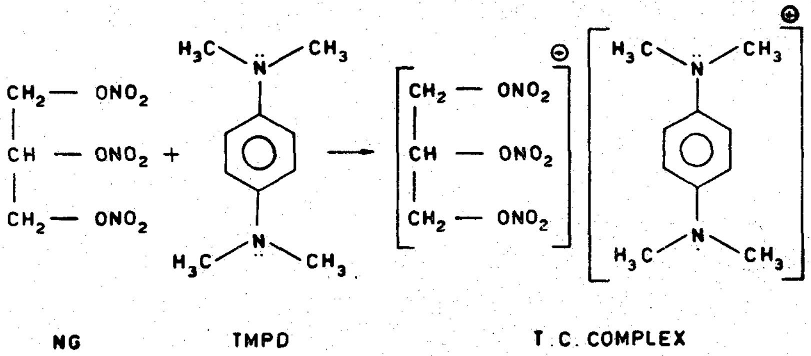

Figure 2. CT complex of NG with TMPD.

Charge Transfer Complex of Tetryl with TMPD

Interaction between tetryl and TMPD was in the molar ratio of 1 : 1 but it formed a solid chargetransfer complex which was isolated and studied by spectroscopy (Fig. 3). It is most likely the result of strong electron delocalization of charge with the benzene nucleus resulting in strong charge accepting property of *C-NO$_2$* group and thereby forming readily chargetransfer complex. When molar solution of tetryl in 1, 2-dichloro-ethane was added to the molar solution of TMPD in the same solvent, an intense bluish-violet colour was first obtained which was slowly changed into brown

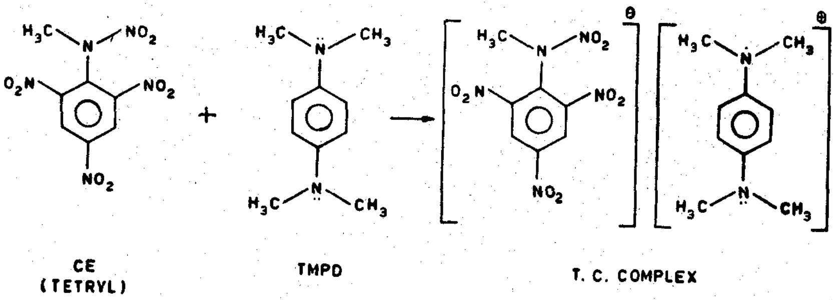

Figure 3. CT complex of CE with TMPD.

colour forming solid charge transfer compound of tetryl-TMPD. The compound was isolated and studied by electronic as well as I.R. spectra.

Charge Transfer Complex of RDX, HMX with TMPD

RDX and HMX are *N-NO_2* compounds and are very weak electron acceptors. Both formed charge transfer complex in 1 : 1 molar ratio. Complexes were formed in solvent and the colour was bluish-violet.

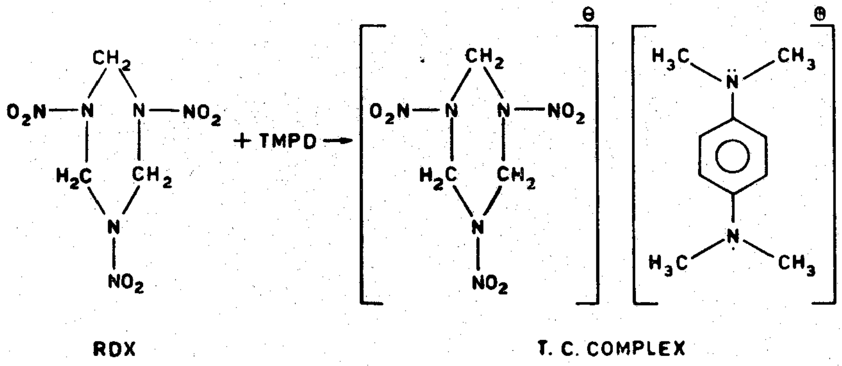

Figure 4. CT complex of RDX with TMPD.

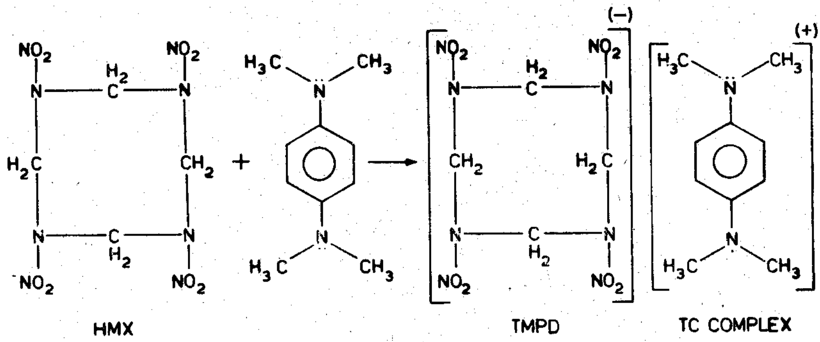

Figure 5. CT complex of HMX with TMPD.

The molar solutions of RDX and HMX in 1, 2-dichloro-ethane was added to the molar solution of TMPD in the same solvent (Figs. 4 & 5). The interaction of these two compounds first produced 'Wurster cation' colour. The electronic spectra showed the characteristic band of Wurster radical which changed with time to yellow colour and gave absorption band characteristic of charge transfer complex. It has been established that this change is typical of solutions in solvents with low dielectric constant such as 1, 2-dichloro-ethane, dichloro-methane and benzene. When RDX or HMX was mixed with TMPD in polar solvents such as methanol or acetone, the original bluish-violet colour remained unchanged and no yellow complex was formed. These complexes are stable in solution and could not be isolated by evaporating the solvent at low temperature and low pressure due to decomposition of nitro compound. Only tarry material was left behind after evaporation.

3. Results and Discussion

Nitro-group as shown in Fig. 6 is positively charged one due to overlapping of *p*-orbitals and electro-negativity of oxygen atoms. An electro-negative substitute *R* removes the electron charge from the nitrogen atom through 6-bond and this inductive loss is compensated by a gain of an equal charge from the π-bond system.

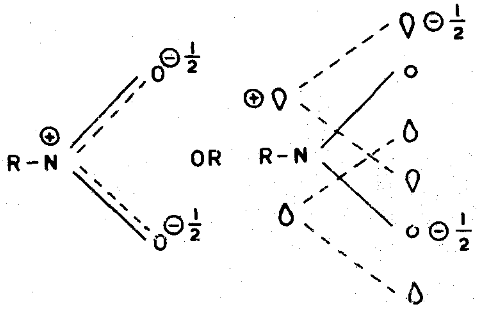

Figure 6. Nitro group.

It is obvious that such a charge is smaller than those resulting from other factors if the entire electron system is considered. This is the reason for nitro compounds to be electron acceptors. In the case of aromatic nitro-compounds there is electron delocalization of the charge with the benzene ring and hence $C\text{-}NO_2$ compounds are strongest electron acceptors and form charge transfer compounds with electron donors such as amines. $O\text{-}NO_2$ and $N\text{-}NO_2$ compounds are very weak electron acceptors as compared to $C\text{-}NO_2$ and that is why their complexes are formed in solutions and cannot be separated but can be identified by electronic and infra-red spectra. We established that at least three $O\text{-}NO_2$ groups are needed to form one Wurster radical with interaction with TMPD. Tetryl formed solid charge transfer complex with TMPD in inert solvent which was identified by I.R. & U.V. spectra because $C\text{-}NO_2$ groups are strong electron acceptors and the two molecules are held together more strongly. RDX and HMX formed charge transfer complexes in solutions only and could not be separated, as they readily decomposed, when solution is evaporated at low temperature and low pressure. We were able to confirm the presence of TMPD cation as well as charge transfer complexes by U.V. as well as infra-red spectroscopy.

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