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A NEW KIND OF CHARGE TRANSFER COMPLEXES.

NITRIC ESTERS AS ELECTRON ACCEPTORS

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One of the authors of the present paper found[2] by way of thermal analysis that D -mannitol hexanitrate /MHN/ and meso-erythritol tetranitrate /ETN/ can form addition complexe with some aromatic compounds. This was later confirmed by one of his co-workers[3]. It was believed that they were charge transfer complexes and it was expected that nitric acid esters are electron acceptors.

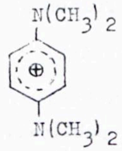
The nature of the complexes now has been studied by spectroscopic techniques and tetramethyl-p-phenylenediamine /TMPD/ was used as electron donor because of its low ionization potential /6.5 eV/. A number of mono-, di-, tri-, tetra- and hexa-O-nitro compounds were examined /Table 1/.

Table 1

Nitric esters	Molar ratio Nitric ester : TMPD	Absorption		
		D_{620}	Concentration of components mol/l	Thickness cm
n-Butyl nitrate	3:1	0.100	0.1	1
sec-Butyl nitrate	3:1	0.158	0.1	1
ter-Butyl nitrate	3:1	0.530	0.1	1
Ethylene glycol dinitrate	3:1	0.410	0.1	1
Glycerol trinitrate /Nitroglycerine,NG/	1:1	0.272	0.18	1
pentaerythritol trinitrate	1:1	0.268	0.22	1
meso-erythritol tetranitrate /ETN/	1:1	0.540	0.01	1
Pentaerythritol tetranitrate /PETN/	1:1	0.100	0.02	1
D -Mannitol hexanitrate /MHN/	1:2	0.499	0.002	0.2
D -Sorbitol hexanitrate	1:2	0.468	0.002	0.2
Dulcitol hexanitrate	1:2	0.455	0.002	0.2
myo-Inositol hexanitrate	1:2	0.530	0.002	0.2

Formation of the donor-cation

It was found that all the nitric esters in solvents: dichloromethane, 1,2-dichloroethane, methanol, acetonitryl, benzene, gave violet colour with TMPD characterised by two absorption bands - 570 and 620 mμ. This indicates that the absorption is due to the presence of Wuster cation /TMPD/ ⁺/I/.



I

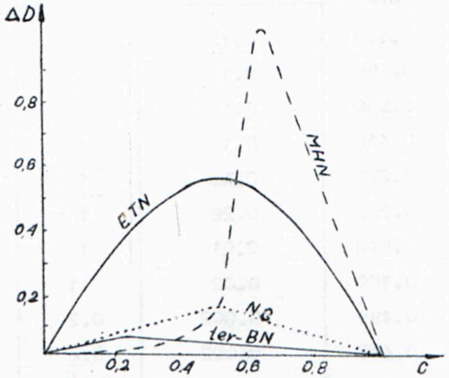
We used the method of continuous changes[4] for the band 620 mμ. Fig. 1 gives the results for butyl nitrates /BN/, nitroglycerine /NG/, ETN and MHN. It follows from the measurements that at least three ONO_2 groups are needed to form Wuster cation. This can be expressed by the equation:

$$xR(ONO_2)_n + yTMPD \rightleftharpoons x/R(ONO_2)_n/^{y\ominus} + y/TMPD/^{\oplus}$$

where R are hydrocarbon groups.

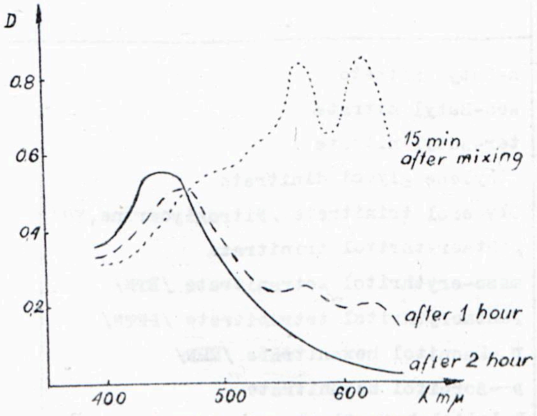
When n = 1 or 2, x = 3, y = 1,
n = 3 or 4, x = 1, y = 1,
n = 6, x = 1, y = 2.

The ability of forming TMPD is the strongest with hexanitrates of hexitols. /The highest absorption figures/. Very weak ability of PETN should be ascribed to its low polarity as pointed out earlier by one of us[5].



Job diagram in 1,2-dichloroethane for ter-BN,NG,ETN /concentrations 0.01 of each, l=1 cm/ and MHN /concentration 0.004, l=0.2 cm/ with TMPD

Fig. 1



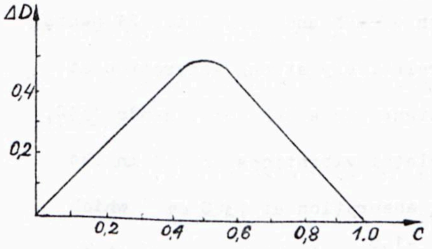
Change with time of electronic spectra of MHN and TMPD in 1,2-dichloroethane at 23°.

Fig. 2

Formation of the charge transfer complex with MHN

More detailed investigation was done with MHN and TMPD. It was found that two maxima 570 and 620 mμ appeared very soon after mixing, but gradually disappeared and a new band was formed at 450 mμ /Fig. 2/. If the violet solution of MHN and TMPD in acetonitryl or methanol is shaken with a solvent of low dielectric constant, such as n-heptane or 1,2-dichloroethane, the latter became coloured yellow - its absorption maximum was at 450 mμ.

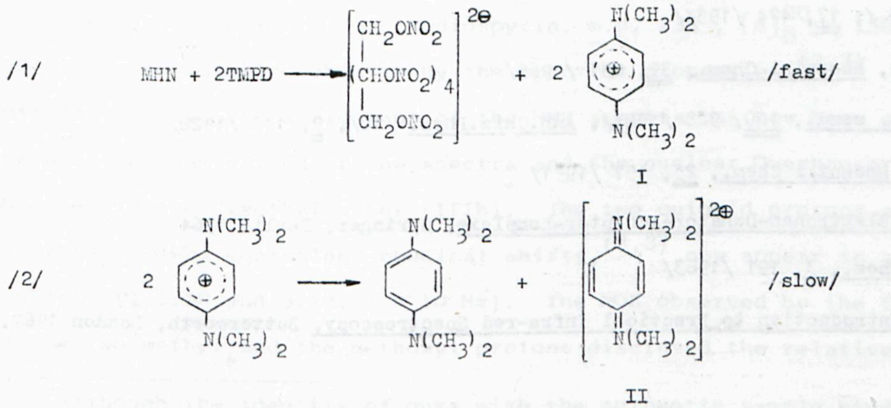
By using the method of continuous changes[4] we established that the molar composition of the complex is 1:1 /Fig. 3/, i.e. the original ratio 1:2 was subject to a disproportionation. By using the Benesi-Hildebrand equation[6] modified for equimolar concentrations we established that the equilibrium constant ^cK of the formation of the complex varies with solvent and decreases with temperature. Thus in 1,2-dichloroethane it has values 59.3 and 27.6 l/mol at 5° and 30° respectively. When in a solvent of high dielectric constant, the complex readily dissociated into ions. This was established by measuring the electric conductivity of the solution in 1,2-dichloroethane: it increased when methanl was added.



Job curve of the complex MHN-TMPD in 1,2-dichloroethane after 24 hours.

Fig. 3

We are suggesting a scheme for the reaction of MHN with TMPD as follows:

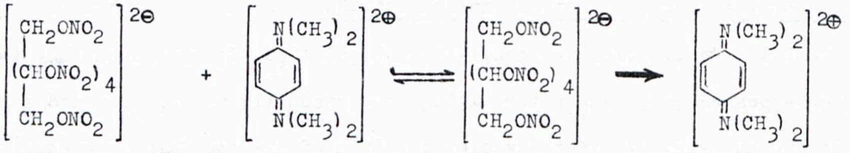


I

II

The formation of charge transfer complex follows. It is probably fast, as an ionic reaction:

/3/



/fast/

Cation II is here stabilized by the weak MHN anion, contrary to the existing data[7] on low stability /II/ in presence of a strong anion.

A detailed kinetic study will be carried out.

However we were unable to isolate the solid complex as it readily decomposed.

When examining the infrared spectrum of the solution of MHN and TMPD after 24 hours, i.e. after the band 450 mμ. fully appeared, we found a relatively strong absorption at 1620 cm^{-1} which does not exist in TMPD and could be assigned to a C=N bond. Bands 1540, 1460 cm^{-1} were also present and could be assigned to skeletal vibrations of C=C in the quinoid ring. The complex gives also a relatively strong absorption at 1360 cm^{-1} which lies in the region of inorganic nitrate ion /1410-1340 cm^{-1}/[8] and which we suggest is due to the negatively charged ONO_2 groups in the MHN anion.

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