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THE SYSTEM LEWIS ACID - NITRO COMPOUND AS A STRONG ELECTRON ACCEPTOR[1]

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In a search for methods of preparing positive ions of aromatic molecules the strong electron affinity of nitro compounds in combination with acids was found.

A very pronounced electron attracting power is displayed by the system aluminium chloride-nitromethane. In a solution of 2% aluminium chloride in nitromethane anthracene is readily converted into the monovalent positive ion (anthracene minus one electron). The green-blue solution exhibits electron spin resonance (ESR) and the UV absorption spectrum is similar to that of the monovalent ion of anthracene (see e.g.[2]).

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*One of us (W.B.) gratefully acknowledges financial support by the Netherlands Organisation of Pure Research (Z.W.O.).

[1] H.M.Buck, Thesis Leyden chapter VI (1959).

[2] W.Y.Aalbersberg, G.J.Hoijtink, E.L.Mackor and W.P.Weijland, J.Chem.Soc. 3049 (1959).

W.Y.Aalbersberg, G.J.Hoijtink, E.L.Mackor and W.P.Weijland, J.Chem.Soc. 3055 (1959).

If 1,1,2,2-tetra(p-methoxyphenyl)ethene is dissolved in such a solution the formation of a divalent positive ion can be demonstrated by comparing the spectrum with that of the perchlorate in nitromethane (fig. 1). From the complete agreement of the two spectra it follows that the ethene has given up two electrons.

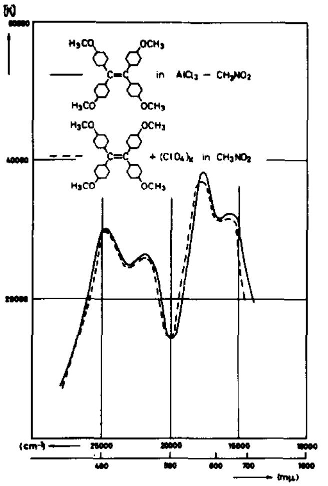

FIG. 1

Similarly 4,4'-dimethoxydiphenyl reacts with aluminium chloride-nitromethane under formation of the monovalent positive ion (fig. 2) *

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*If the concentration of 4,4'-dimethoxydiphenyl is small the solution is red and the UV absorption is completely different from the monovalent positive ion. It may be of interest to note that this absorption band may be related to the small band at the same position in the spectrum of the irradiated solution of 4,4'-dimethoxydiphenyl in boric acid glass (fig. 2).

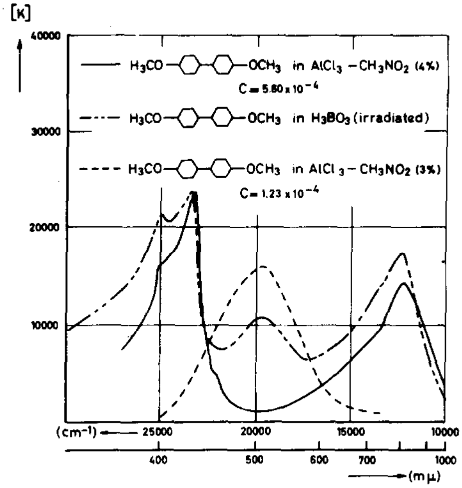
[K]
40000
30000
20000
10000
H₃CO–⬡–⬡–OCH₃ in AlCl₃ – CH₃NO₂ (4%)
C = 5.80 x 10⁻⁴
H₃CO–⬡–⬡–OCH₃ in H₃BO₃ (irradiated)
H₃CO–⬡–⬡–OCH₃ in AlCl₃ – CH₃NO₂ (3%)
C = 1.23 x 10⁻⁴
(cm⁻¹)
25000
20000
15000
10000
400
500
600
700
1000
(mμ)

FIG. 2

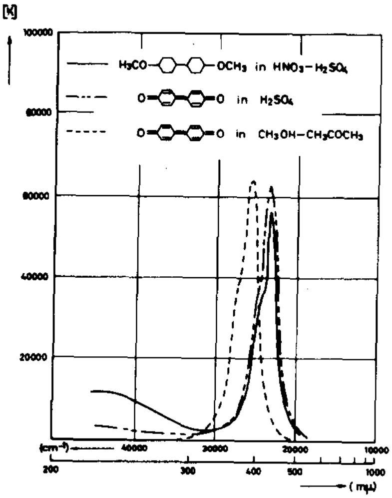
[K]
100000
80000
60000
40000
20000
H₃CO–⬡–⬡–OCH₃ in HNO₃ – H₂SO₄
O=⬡=⬡=O in H₂SO₄
O=⬡=⬡=O in CH₃OH – CH₃COCH₃
(cm⁻¹)
40000
30000
20000
10000
200
300
400
500
1000
(mμ)

FIG. 3

This solution exhibits strong ESR. The same reaction occurs in a solution of aluminium chloride in nitrobenzene, although in general nitrobenzene-aluminium chloride is less active than nitromethane-aluminium chloride.

An even stronger electron abstracting power is displayed by the system nitric acid-sulphuric acid. This could be established by dissolving 4,4'-dimethoxydiphenyl in sulphuric acid containing a small amount of nitric acid or by dissolving the dark blue molecular compound 4,4'-dimethoxydiphenyl.2 HNO_3[3] in sulphuric acid.[4] The yellow solution contains the divalent positive ion as appears from the UV absorption spectrum (fig. 3).

It was also observed that the addition of a small amount of nitromethane to sulphuric acid gives rise to a solution with strong electron acceptor properties. Triphenylene in sulphuric acid is colourless but if some nitromethane is added the solution turns blue. This solution, however, exhibits no ESR. Triphenylene in aluminium chloride-nitromethane gives a paramagnetic solution and the UV absorption spectrum shows some similarity to that of the monovalent ion.[5]

With aromatic hydrocarbons having a low ionisation energy the activity of a solution of aluminium chloride in nitromethane may be

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[3] J.van Alphen, Recueil **49**, 771 (1930).

[4] H.M.Buck, Thesis Leyden chapter III (1959).

[5] P.Balk, G.J.Hoijtink and J.W.H.Schreurs, Recueil **76**, 813 (1957).

too high, leading to secondary reactions. With perylene the formation of the monovalent positive ion in aluminium chloride-nitrobenzene could easily be demonstrated. The UV spectrum characteristic of the monovalent positive ion[2] remains nearly unchanged for days. The solution in aluminium chloride-nitromethane, however, is very unstable and neither the monovalent positive ion nor the divalent positive ion could be found. If the activity of the solution was lowered by the addition of carbon tetrachloride the monovalent positive ion could be identified.

In all our experiments the formation of the monovalent positive ions was checked, if possible, by ESR measurements and by comparing the UV absorption spectra with known absorption spectra of the monovalent and divalent negative or positive ions.[5,6]

Apart from the acids and nitro compounds mentioned a large number of other acid-nitro compound systems have been studied with respect to various aromatic compounds. The results of these experiments together with results on the influence of temperature and irradiation will be published elsewhere.

In general it was found that most aromatic hydrocarbons dissolved in nitromethane, to which a small amount of aluminium chloride has been added, give coloured solutions. For instance benzene dissolves

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[6] P.Bennema, G.J.Hoijtink, J.H.Lupinski, L.J.Oosterhoff, P.Selier and J.L.W.van Voorst, <u>Mol.Phys</u>. **2**, 431 (1959)

with an orange colour, naphthalene gives a red solution. In neither solution could ESR be detected. The correlation between the ionisation energy of the aromatic molecule and the bathochromic shift of the colour of the solution suggests the formation of charge transfer complexes as was first pointed out by Wizinger.[7] The appearance of colour on the addition of benzene to a solution of aluminium chloride-nitromethane was also observed by Schmerling.[8] Similar observations have been made by H.C.Brown and Grayson[9] for a number of aromatic hydrocarbons with aluminium chloride-nitrobenzene. According to these authors it would appear that the aluminium chloride greatly increases the electrophilic character of the nitrobenzene molecule and brings about stable complex formation with aromatic hydrocarbons of high basicity. In view of our experiments it seems reasonable to assume that in general the combination acid-nitro compound must be considered as an electron acceptor.

In connection with the phenomena discussed in this paper it may be of interest to mention the characteristic colour of solutions of substituted benzenes and nitric acid in nitromethane which were observed by Ingold et al.[10] Our experiments suggest that these colours are to be ascribed to charge transfer complexes. The correlation

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[7] R.Wizinger, Organische Farbstoffe 48-51 (1933).

[8] L.Schmerling, Ind.Eng.Chem. **40**, 2072 (1948).

[9] H.C.Brown and M.Grayson, J.Amer.Chem.Soc. **75**, 6285 (1953).

[10] G.A.Benford and C.K.Ingold, J.Chem.Soc. 929 (1938).

between colour and nitration velocity found by Ingold et al. suggests that the formation of a charge transfer complex may be an essential step in the nitration process (cf. R.D.Brown[11]).

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[11] R.D.Brown, J.Chem.Soc. 2224 (1959).