Tetrahedron Vol. 42, No. 14, pp. 4089 to 4092, 1986
Printed in Great Britain.

0040-4020/86 $3.00+.00
Pergamon Journals Ltd.

OXIDATION OF AROMATIC AMINES WITH CHROMYL CHLORIDE—II

STUDIES ON THE INTERMEDIATE SOLID ADDUCTS

C. NALLAIAH*
Department of Chemistry, Imo State University, Etiti, Imo State, Nigeria

and

J. A. STRICKSON
North East Surrey College of Technology, Reigate Road, Ewell, Epsom, Surrey KT17 3DS, U.K.

(*Received in UK* 9 *July* 1984)

Abstract—Oxidation of aromatic primary amines with chromyl chloride results in the formation of intermediate solid Etard adducts (C. Nallaiah and J. A. Strickson, *Tetrahedron* **42**, 4083 (1986)). Elemental analysis of the adducts indicates that the anilines, which give 1,4-benzoquinone anils in good yields, form adducts close to a 1 : 1 stoichiometry with the oxidant while those forming 1,4-benzoquinones in substantial yields form 1 : 2 adducts. Magnetic measurements on the adducts reveal that chromium atoms are mainly present in the oxidation state chromium(IV). IR studies indicate that the adducts comprise of 1,4-benzoquinone imines and di-imines as ligands and that giant molecules are formed by chloro and hydroxy bridges.

Etard reaction of hydrocarbons and phenols are well documented.[2,3] The lack of firm structural information, however, has prevented a clear understanding of the nature of Etard adducts. The exothermicity and colour changes that accompany Etard reaction and also magnetic and ESR studies strongly suggest changes in the oxidation state of chromium in the adduct.

RESULTS AND DISCUSSION

The colour of the adducts formed with anilines, depends on the nature and position of the substituents in the ring. The adducts of methyl substituted anilines were generally deep brown in colour while those of halo-substituted anilines had various colours ranging from deep violet (adduct of 2,4,6-tribromoaniline) to greenish blue (adduct of 2,4,6-trichloroaniline).

Like other Etard adducts, aniline adducts were found to be completely insoluble in non-polar solvents and reacted irreversibly with polar solvents. Insolubility of the adducts prevented examination of the solution spectra of the adducts. The IR spectra of the adducts were recorded in the solid state using KBr discs. The spectra of adducts which on hydrolysis gave high yields of discrete organic products had more defined sharp absorption bands than those adducts which yielded mainly polymeric materials. The spectra in the regions 1550–1650 cm^{-1} and 650–300 cm^{-1} were remarkably similar in most of the adducts. A broad absorption band in the 3300–3450 cm^{-1} region was observed in all the adducts and was assigned to hydroxy and imino groups.[4–6] All the adducts had strong absorption bands in the 530–560 cm^{-1} and 340–360 cm^{-1} regions. The former bands could be assigned to either Cr–OH or Cr–O–Cr vibrations,[4,7] while the latter could be assigned to Cr–Cl. Weak absorption bands also appeared in the 300–280 cm^{-1} region which could be assigned to terminal Cr–Cl and bridged Cr–Cl–Cr groups.[4,8] The spectra of the adducts obtained when the KBr discs were made under normal laboratory conditions instead of under anhydrous conditions (i.e. using a dry box), were remarkable. In most cases additional absorption bands appeared in the 1660–1685 cm^{-1} region, characteristic of α,β-unsaturated carbonyl compounds. This could be attributed to hydrolysis of imino groups to carbonyl groups.

Elemental analyses of the adducts indicated that anilines which gave quinones as the major product on hydrolysis formed adducts close to a 1 : 2 (aniline–oxidant) stoichiometry, while those that formed quinone anils as the major product formed adducts close to a 1 : 1 stoichiometry (Table 1). Anilines which formed a high proportion of polymeric materials, formed non-stoichiometric adducts.

Magnetic studies on the adducts were carried out to determine the oxidation state of the chromium atoms. The magnetic susceptibility (x_m) of the adducts measured at 298 K and the effective magnetic moment (μ_{eff}) corresponding to these values are presented in Table 2. The molar susceptibilities of 2,4,6-trichloroaniline and 3,5-dimethylaniline adducts were investigated over the range 113–273 K. These two adducts were chosen as the representative adducts for 1 : 1 and 1 : 2 adducts, respectively. The exhibited normal magnetic behaviour (i.e. obeying the Curie–Weiss law) (Figs 1 and 2) and, consequently, the Weiss constants were found to be low (6.43 and 7.10, respectively). It has been shown that, in the case of polynuclear chromium complexes with one or more bridging groups, the interaction between metal centres via the ligands is reflected by high Weiss constants. However, for chromium compounds containing hydroxy and chloro bridges, such interactions have been shown to be very small and these decrease with increasing multiplicity of the bridging groups.[9] The average value of the effective magnetic moment of chromium atoms in the aniline adducts varied between 3.07 and 3.3 BM (Table 2). In contrast to the values obtained for chromium atoms in substituted anilines,

Table 1

Aniline adduct	Found (%) N	Found (%) Cr	Calc for 1:1 adduct (%) N	Calc for 1:1 adduct (%) Cr	Calc for 1:2 adduct (%) N	Calc for 1:2 adduct (%) Cr	Major oxidation product
Aniline	4.71	21.63	5.64	24.96	3.47	25.81	Polymer
2-Methyl-	2.97	21.43	5.34	19.84	3.28	24.94	Polymer
4-Methyl-	3.62	19.85	5.34	19.84	3.28	24.94	Quinone
2,6-Dimethyl-	5.65	16.78	5.07	18.83	3.24	24.12	Quinone anil
2,4-Dimethyl-	2.68	20.71	5.07	18.83	3.24	24.12	Quinone
3,4-Dimethyl-	3.05	23.51	5.07	18.83	3.24	24.12	Quinone
3,5-Dimethyl-	3.46	21.72	5.07	18.83	3.24	24.12	Quinone
2,4,6-Trimethyl-	3.52	18.47	4.83	17.93	3.15	23.37	Quinone anil
2,4,5-Trimethyl-	3.41	18.39	4.83	17.93	3.15	23.37	Quinone
2-Chloro-	3.03	20.37	4.95	18.42	3.20	23.77	Polymer
4-Chloro-	3.88	19.57	4.95	18.42	3.20	23.77	Quinone anil
2,6-Dichloro-	3.02	15.73	4.42	16.40	2.99	22.04	Quinone anil
2,4-Dichloro-	3.63	18.07	4.42	16.40	2.99	22.04	Quinone
2,5-Dichloro-	3.92	15.44	4.42	16.40	2.99	22.04	Quinone anil
2,4,6-Trichloro-	3.81	12.02	3.98	14.79	2.76	20.53	Quinone anil
2,4,5-Trichloro-	3.59	11.34	3.98	14.79	2.76	20.53	Quinone anil
4-Bromo-	3.17	18.27	4.28	15.90	2.90	21.57	Quinone anil
2-Bromo-	3.97	17.38	4.28	15.90	2.90	21.57	Polymer
2,4-Dibromo-	2.84	10.68	3.45	12.81	2.49	18.54	Quinone
2,6-Dibromo-	2.91	11.53	3.45	12.81	2.49	18.54	Quinone anil
2,5-Dibromo-	2.98	12.08	3.45	12.81	2.49	18.54	Quinone anil
2,4,6-Tribromo-	2.68	9.71	2.89	10.72	2.19	16.26	Quinone anil

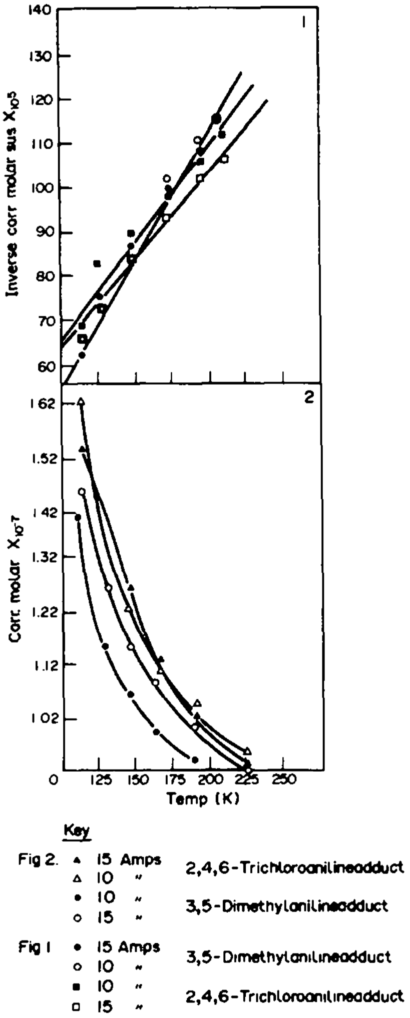
the value for an unsubstituted aniline adduct was found to be high (3.80 BM).

The effective magnetic moment of chromium atoms in toluene adducts[10] was 3.18 BM which corresponds to two unpaired electrons [i.e. chromium(IV)]. That of phenol adducts did not even approximately correspond to the spin-only value for either chromium(III) or chromium(IV) but was somewhere in between.[4] The values obtained for aniline adducts indicate that chromium atoms were present largely in the chromium(IV) state thus demonstrating that a substantial part of the oxidation had been completed by the time the solid adduct precipitated.

The hydrolysis of the adduct obtained from 2,4,6-

Table 2

Aniline adduct	χ_m m^3/mol $\times 10^{-8}$	μ_{eff} Cr (BM)	No. of unpaired electrons (n)
Aniline	7.6560	3.8	3.0
2-Methylaniline	4.9871	3.07	2.0
4-Methylaniline	5.0319	3.08	2.0
2,6-Dimethylaniline	5.0370	3.09	2.0
2,4-Dimethylaniline	5.1840	3.13	2.0
3,4-Dimethylaniline	5.1870	3.13	2.0
3,5-Dimethylaniline	5.0968	3.10	2.0
2,4,6-Trimethylaniline	4.9772	3.07	2.0
2,4,5-Trimethylaniline	5.0103	3.08	2.0
2-Chloroaniline	5.4438	3.21	2.0
4-Chloroaniline	5.1127	3.11	2.0
2,6-Dichloroaniline	5.4628	3.21	2.0
2,4-Dichloroaniline	5.6112	3.26	2.0
2,5-Dichloroaniline	5.3764	3.19	2.0
2,4,6-Trichloroaniline	5.5205	3.23	2.0
2,4,5-Trichloroaniline	5.4657	3.22	2.0
4-Bromoaniline	5.2180	3.14	2.0
2-Bromoaniline	5.3246	3.17	2.0
2,4-Dibromoaniline	5.3927	3.19	2.0
2,6-Dibromoaniline	4.9738	3.07	2.0
2,5-Dibromoaniline	5.2380	3.15	2.0
2,4,6-Tribromoaniline	5.3816	3.19	2.0



Figs 1 and 2.

trimethylaniline (this adduct gave the highest yield of quinone anil and the lowest yield of polymeric material)[1] with water enriched with heavy oxygen (^{18}O) gave the corresponding quinone anil and the quinone which contained a high proportion of heavy oxygen (Experimental). This clearly suggests that the oxygen atom of the quinone anil and one of the oxygens of the quinone are derived from water during hydrolysis. This also indicates the presence of quinone imines and di-imines in the adducts.

The proposed structures for the 1 : 1 and 1 : 2 adducts are shown in Figs 3 and 4, respectively. The chromium atoms can easily acquire a stable co-ordination number of six by utilizing the quinone imines and di-imines as ligands. Giant molecules can be formed by chloro and hydroxy bridges and this could account for the precipitation of the solid adducts. The IR, magnetic and elemental analyses data are consistent with the proposed structures.

EXPERIMENTAL

Most of the details have been described previously.[1] Magnetic measurements were made using a variable temp Gouy balance, manufactured by Newport Instruments and calibrated for a range of magnetic fields using $Hg[Co(CNS)_4]$ as standard. Magnetic currents of 10 and 15 A were used, corresponding to magnetic fields of 5.65 and 6.59 kGauss, respectively.

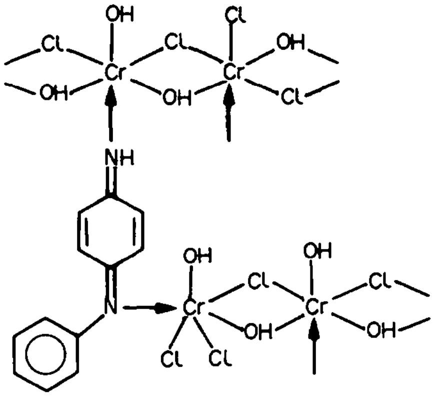


Fig. 3.

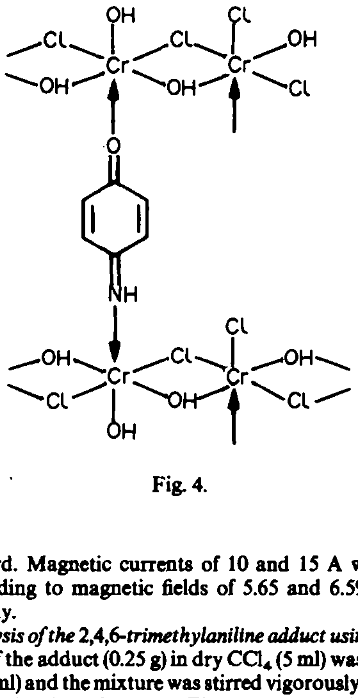


Fig. 4.

Hydrolysis of the 2,4,6-trimethylaniline adduct using $H_2{}^{18}O$. A slurry of the adduct (0.25 g) in dry CCl_4 (5 ml) was added to $H_2{}^{18}O$ (1 ml) and the mixture was stirred vigorously by means of a magnetic stirrer for 1.5 h. The temp was maintained at 0–5° by external cooling.

The deep red CCl_4 layer was separated and dried overnight with Na_2SO_4. The mixture was filtered and evaporated to dryness under reduced pressure. The reddish purple residue was chromatographed on silica gel using petroleum ether–EtOAc (7 : 1).

The fast running yellow band on evaporation and recrystallization from MeOH gave yellow crystals of 2,6-dimethyl-1,4-benzoquinone: m.p. 72–73° (lit 73°); ^1H-NMR (CCl_4): δ 3.55 (3H, s), 8.05 (6H, s); IR ν_{max}^{KBr} cm^{-1}: 1660, 1645; $[M]^+$ m/z 138 (27% of the base peak at m/z 108).

The slow running deep reddish purple band on evaporation and recrystallization from MeOH gave deep reddish purple crystals of 2,6-dimethyl-1,4-benzoquinone-4-(2,4,6-trimethyl anil): m.p. 95–96° (lit 97°); ^1H-NMR (CCl_4): δ 2.84 (1H, m), 3.17 (2H, s), 3.60 (1H, m), 7.73 (3H, s), 7.91 (3H, d), 8.08 (3H, d), 8.13 (6H, s); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1655, 1560; $[M]^+$ m/z 255 (30% of the base peak at m/z 225).

Acknowledgements—We should like to thank Kingston Polytechnic, U.K., for providing research facilities and the Royal Borough of Kingston-on-Thames for financial assistance.

REFERENCES

[1] C. Nallaiah and J. A. Strickson, *Tetrahedron* **42**, 4083 (1986).
[2] F. Freeman, *Rev. React. Species Chem. React.* 37 (1972).
[3] W. H. Hartford and M. Darrin, *Chem. Rev.* **58**, 1 (1958).
[4] M. J. Leigh and J. A. Strickson, *J. Chem. Soc. Perkin Trans. 2* 1476 (1973).
[5] Barns, Liddel and Williams, *Ind. Eng. Chem. Anal. Ed.* **15**, 456 (1943).
[6] Randall, Fuson, Flower and Dangl, *Infra-red Detection of Organic Structures*. Van Nostrand, New York (1940).
[7] H. D. Hawkin and W. P. Griffiths, *J. Chem. Soc. A* 472 (1966).
[8] D. M. Adams, J. Chatt, J. M. Davidson and J. Gerratt, *J. Chem. Soc.* 2189 (1963).
[9] A. Earnshaw and J. Lweis, *Ibid.* 396 (1961).
[10] O. H. Wheeler, *Can. J. Chem.* **38**, 2137 (1960).