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## THE SOLVENT EFFECT IN THE USE OF CHLORANIL AS A REAGENT IN THE IDENTIFICATION OF AROMATIC AMINES ON SILICA GEL THIN LAYERS

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### SUMMARY

The identification of aromatic amines on Silica Gel G and thin-layer aluminium sheets Silica Gel F<sub>254</sub> plates using chloranil (2,3,5,6-tetrachloro-1,4-benzoquinone) is investigated, showing that colour intensity depends on the solvent used on chloranil. The coloured compound aromatic amine-chloranil is produced due to " $\pi$ -electron" type compound formation, owing to the interaction between amines and silica gel acid groups.

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### INTRODUCTION

The use of chloranil (2,3,5,6-tetrachloro-1,4-benzoquinone) as intermediate in obtaining synthetic dyes is well known. The diarylaminobenzoquinones produced by condensing chloranil with aromatic amines and from which oxazines are obtained by oxidation (cyclisation), allow the production of deeply coloured compounds.

This reagent was first used by LE ROSEN *et al.*<sup>1</sup> in the chromatography of aliphatic amines, without widespread knowledge. The use of halogen-quinone derivatives as detection reagents<sup>2</sup> for amines and other aromatic hydrocarbon derivatives has been recently developed; however, they failed to be efficient for the identification of certain aromatic amines.

The high reactivity<sup>3</sup> of chloranil makes it an ideal reagent for identification of aromatic amines found in coal tars and similar compounds thanks to its faculty for condensation with amines, phenols, thiols, etc. This is the reason for choosing this reagent.

### MATERIALS AND METHODS

The aromatic amines used here are standard grade material from Matheson, Coleman and Bell, without any purification. We used benzene-ethanol (5:1) and pure benzene as solvents.

The first tests were carried out on 20 × 20 cm glass plates prepared with Silica Gel G from E. Merck with a Desaga spreader and activated about 1 h at 100–110°.

We also observed its behaviour on aluminium plates of the type TLC aluminium sheets—Silica Gel F<sub>254</sub>, 20 × 20 cm (0.25 mm).

The chloranil (2,3,5,6-tetrachloro-1,4-benzoquinone) used was obtained from E. Merck(p.A. grade) and was dissolved in: (a) ethanol—a saturated and filtered solution; (b) *n*-butanol—a saturated and filtered solution; (c) acetone—a saturated and filtered solution; (d) monochlorobenzene—a 0.2% solution; (e) chloroform—a saturated and filtered solution.

The chromatograms of the aromatic amines after development in benzene-ethanol (5:1) were sprayed with each of the above solutions; the 0.2% chloranil solution gave the best results.

The already developed plates were dried at room temperature and then sprayed with a freshly prepared solution of chloranil in monochlorobenzene. We noticed that the spots showed up immediately.

TABLE I  
COLOURS OBTAINED FOR AROMATIC AMINES  
0.2% chloranil solution on Silica Gel G plates.

No.	Aromatic amine	<i>R<sub>F</sub></i> values		Reaction with chloranil (monochlorobenzene) <sup>a</sup>
		Benzene	Benzene-ethanol	
1	Aniline	0.42	0.48	YBr dull
2	<i>o</i> -Chloroaniline	0.78	0.60	YP pale
3	<i>m</i> -Chloroaniline	0.67	0.53	Y (I)
4	<i>p</i> -Chloroaniline	0.56	0.50	YBr
5	<i>o</i> -Fluoroaniline	0.64	0.58	YP pale
6	<i>m</i> -Fluoroaniline	0.55	0.50	Y (I)
7	<i>p</i> -Fluoroaniline	0.38	0.48	YBr dull
8	<i>m</i> -Bromoaniline	0.58	0.53	Y (I)
9	<i>p</i> -Bromoaniline	0.53	0.50	YBr
10	<i>o</i> -Toluidine	0.41	0.55	GrG
11	<i>m</i> -Toluidine	0.35	0.51	YBr dull
12	<i>p</i> -Toluidine	0.30	0.46	Br
13	<i>o</i> -Anisidine	0.75	0.56	YBr
14	<i>m</i> -Anisidine	0.38	0.50	YBr dull
15	<i>p</i> -Anisidine	0.23	0.43	YBr
16	<i>o</i> -Aminophenol	0.03	0.34	Or
17	<i>m</i> -Aminophenol	0.02	0.29	Br
18	<i>p</i> -Aminophenol	0	0.15	Br
19	<i>o</i> -Nitroaniline	0.46	0.47	Y (I)
20	<i>m</i> -Nitroaniline	0.35	0.41	Y pale
21	<i>p</i> -Nitroaniline	0.22	0.28	Y
22	2,4-Xylidine	0.50	0.53	Y
23	2,5-Xylidine	0.59	0.58	GrY
24	Carbazole	0.88	0.62	V (I)
25	9-Ethylcarbazole	0.96	0.70	V (I)
26	N,N'-Diethylaniline	0.81	0.68	GrB dull
27	Benzidine	0.06	0.45	YBr
28	1-Naphthylamine	0.33	—	Y dull
29	N-Ethyl-1-naphthylamine	0.65	0.68	BG
30	Acetoaniline	n	n	—
31	Aminoacetoaniline	0.01	0.19	Br
32	Diphenylamine	0.58	0.67	B
33	Dimethyl- <i>p</i> -phenylenediamine	0.02	0.38	GrG

<sup>a</sup> Colours: B = blue; Br = brown; Gr = green; G = grey; Or = orange; V = violet; Y = yellow; I = intense; P = purple; n = no reaction.

Table I shows the colours obtained for a series of aromatic amines using the chloranil solution, and also the  $R_F$  values for the benzene and benzene-ethanol (5:1) systems.

The diazotisation and coupling reactions with the amines were carried out by spraying the plates with a mixture of equal parts of HCl and  $\text{NaNO}_2$  solutions, both 5%. The plates and the spots were checked 2 and 24 h after nitrous acid application and allowing them to stand under laboratory conditions.

To ensure uniformity in the description of the colours the "Hue Indication Chart" from the Colour Index<sup>4</sup> was used as reference.

## RESULTS

The reactivity of the chlorine atoms of chloranil (2,3,5,6-tetrachloro-1,4-benzoquinone) is exhibited more readily by the atoms in the *para* (2,5) position than by those in the *meta*. Consequently the chloranil condensation reaction with aromatic amines goes through nucleophilic substitution, resulting in primarily aryl-amine-benzoquinone derivatives, which after oxidative cyclisation produce the respective dioxazines. The quinoid dyes thus obtained display very intense colours.

Both primary and secondary amines react with chloranil in monochlorobenzene solution on the silica gel layer, giving deeply coloured spots directly related to each type of substituted derivative from aniline. The resulting colours from the reaction chloranil-aromatic amine are shown in Table I; it can be observed that the *ortho* derivatives always display a weaker colour than the respective *meta* and *para* isomers, the *para* being more deeply coloured than *meta* derivatives. An intense colour was only obtained on the plate when monochlorobenzene was used as the chloranil solvent. Other solvents did not give the same result, except with carbazole, diphenylamine and *o*-chloroaniline, which after 24 h, produced a decrease in colour intensity.

However, this colour reaction between chloranil and aromatic amines does not take place on cellulose plates (of the type TLC aluminium sheets-cellulose; Merck AG) even with a chloranil solution in monochlorobenzene.

The sensitivity of the chloranil-aromatic amines reaction on silica gel plates was found to be about 0.01  $\mu\text{g}$ , as shown in Table II.

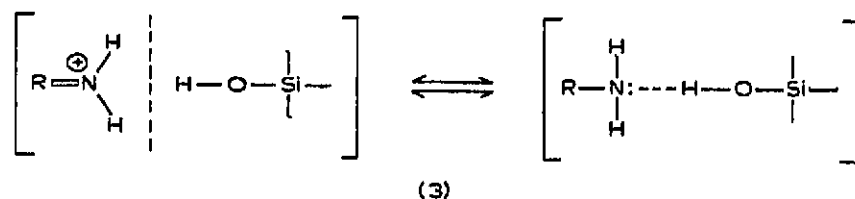
TABLE II

DETECTION OF AROMATIC AMINES ON SILICA GEL G PLATES USING A 0.2% CHLORANIL SOLUTION IN MONOCHLOROBENZENE

Aromatic amine	$\mu\text{g}$ detected	Colour on the plate
<i>o</i> -Chloroaniline	0.01	no reaction
	0.02	pale lilac
<i>o</i> -Anisidine	0.01	olive
	0.02	olive
$\text{N,N}'$ -Dimethylaniline	0.01	violet
	0.02	violet
Diphenylamine	0.01	no reaction
	0.02	pale lilac

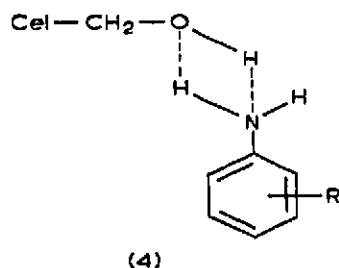


resulting from the equilibrium between the possible forms



where the hybrid ion formation as in (2) is due to the proton provided by the silica gel.

The alcoholic character of the cellulose hydroxyl (R-OH) does not permit the existence of this protonised system (*polar* form 2). In this case, only a hydrogen bond of the type:



occurs, whose unpolarised form does not react with chloranil.

Since the polar form shown in (2) is thought to be responsible for the colour reaction between aromatic amines and chloranil and only occurs on Silica Gel G plates, we tried to prove its existence by using the amine diazotisation and coupling reaction.

We know that coupling of amines with diazonium salts comes about from their very stable R-NH<sub>2</sub> form, and not from the *cationic* form R-NH<sub>3</sub><sup>+</sup>. Now, if we compare the polar character of form (2) with the non-polarized form resulting from chromatographic development over cellulose plates (4), we note that only form (2) can be diazotised and coupled with itself, while form (4) is only capable of diazotisation and subsequent coupling with a coupling agent, due to intermolecular hydrogen bonds.

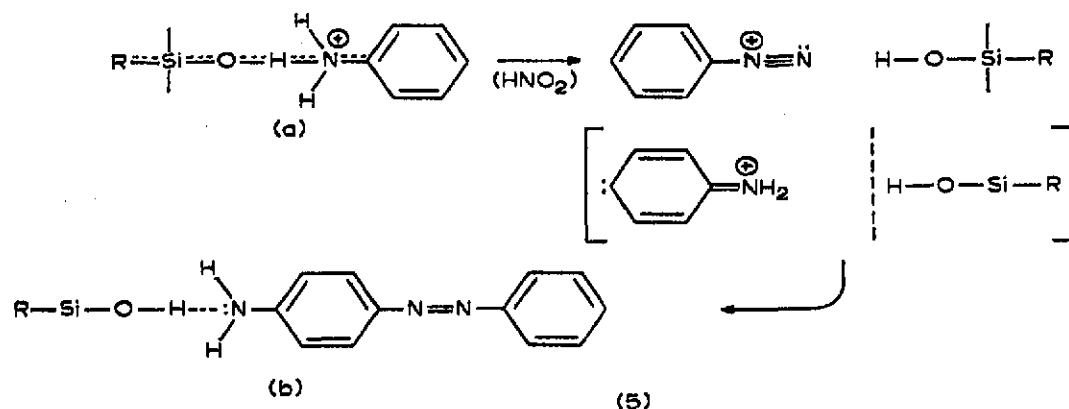
This was proved by chromatographing some of the amines on Silica Gel G and

TABLE III

AROMATIC AMINES AND NITROUS ACID REACTION ON SILICA GEL PLATES

Amine	Reaction with HNO <sub>2</sub>	
	Silica gel	Cellulose
<i>o</i> -Chloroaniline	YBr pale	—
<i>o</i> -Anisidine	RBr	—
<i>m</i> -Chloroaniline	RY	—
<i>o</i> -Fluoroaniline	RGr pale	—
<i>m</i> -Bromoaniline	YBr dull	—
<i>p</i> -Chloroaniline	RBr	—
<i>m</i> -Fluoroaniline	Br	—
<i>p</i> -Bromoaniline	RBr	—
<i>o</i> -Nitroaniline	Y dull	Y
Aniline	RBr	—

cellulose plates and then developing them with nitrous acid (*vide* experimental part). The results are shown in Table III; where it can be seen that simply by applying nitrous acid solution diazotisation and coupling with in the amine occurs. A possible mechanism could be as follows:



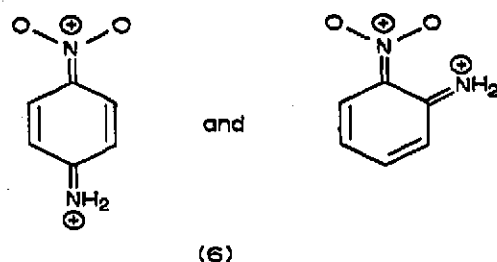
The monoazo compound thus obtained (5.b) results from the initial form (5.a).

This mechanism does not occur with cellulose plates because the stable form (4) does not permit the existence of an intermediate situation like (2).

Chromatograms containing azo dyes obtained after diazotisation and *auto*-coupling reactions and a main dye component which was shown to be deeply coloured after extraction from the plates.

Some dyes of the type (5.b) were also chromatographed, showing that for those amines giving only one dye, due to the existence of a single coupling position (*ortho*-anisidine and such like), we only found the *para* coupled derivative. However, *meta*-fluoraniline with free *ortho* and *para* positions, gave two spots on the chromatogram, one yellowish-orange and the other yellow (respectively  $R_F = 0.68$  and  $R_F = 0.56$ ). Aniline also gave two coloured spots, one yellow ( $R_F = 0.51$ ) and the other orange ( $R_F = 0.57$ ) in a lesser quantity for the same reason.

The reaction presented in 5 does not occur with nitroanilines, because the structures



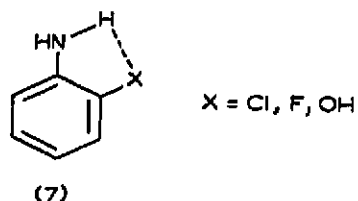
do not allow the monoazo dye development. The nitroanilines produce only their respective diazo compounds, which couple with a  $\beta$ -naphthol solution, giving the corresponding monoazo dye.

#### *Development of the chloranil-aromatic amine coloured compounds*

Since coloured compounds only develop between chloranil and aromatic amines on silica gel supports, we may conclude the existence of a compound of the  $\pi$ -complex

type resulting from the contribution of the polar character of form (2). The absence of a colour reaction on cellulose supports can only be justified by the existence of such a compound.

Such complexes are known in thin-layer chromatography, mainly relating to aromatic amines, whose electron-donor character contributes to the development of these complexes. The colour of the complex so obtained is closely related to the type of substituent present in the aromatic amine. In the case of those amines substituted in the *ortho* position, when the substituent is capable of forming an intramolecular hydrogen bond of the type,



which contributes to this molecule being less polar and causes a decrease in promotes in the colour intensity of the complex (Table I) in relation to the *meta* and *para* derivatives, which are deeply coloured. In nitroanilines, the *ortho* and *para* derivatives

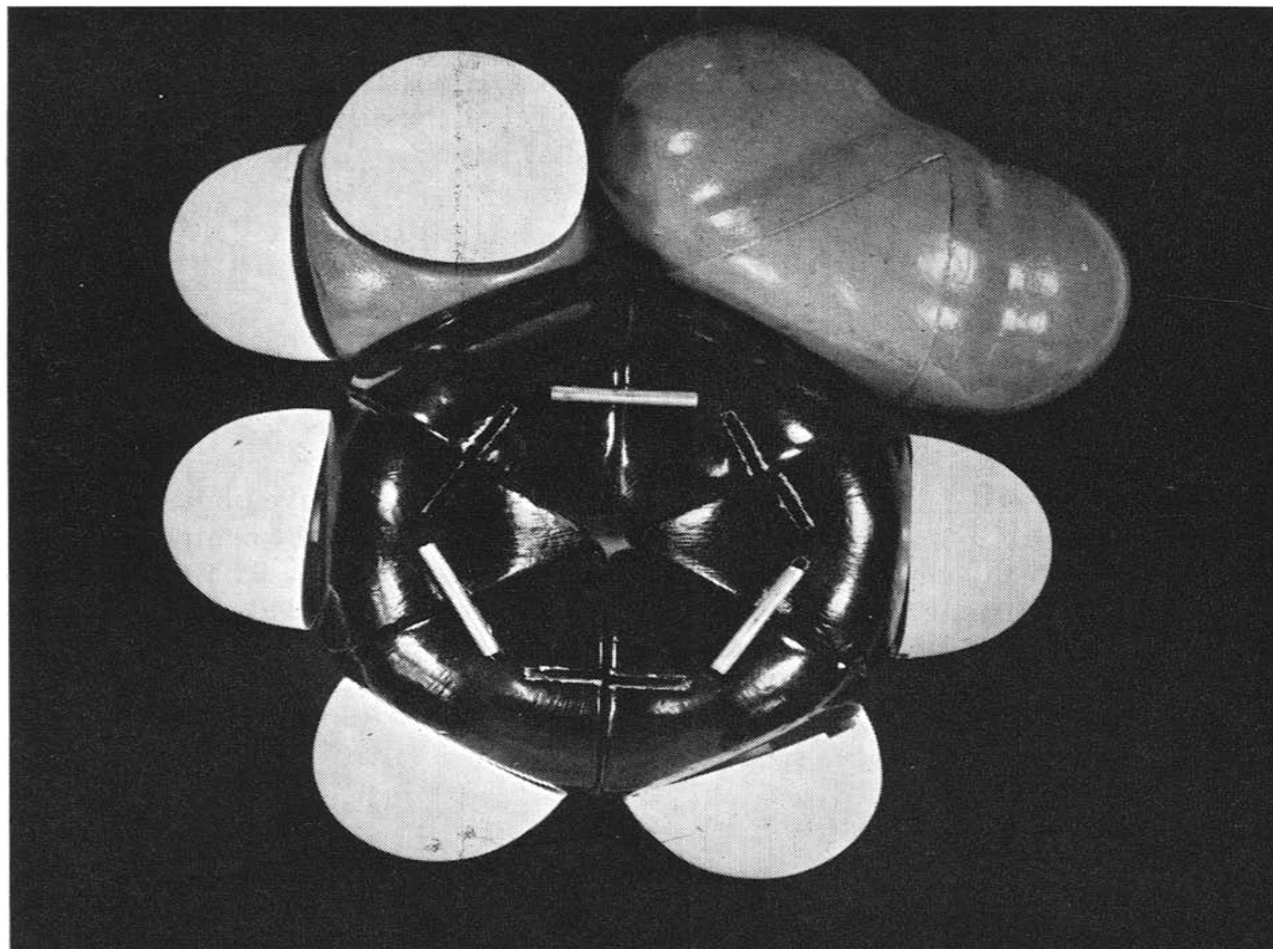
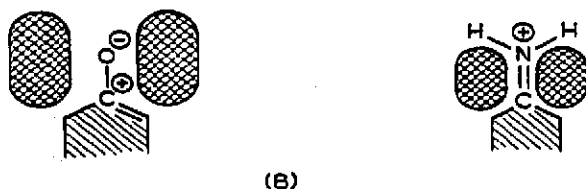


Fig. 2. Molecular model of *o*-nitroaniline.

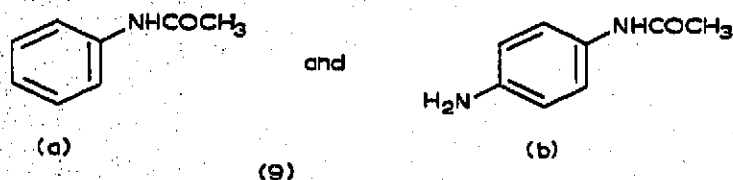
give an intense yellow colour with chloranil, while the *meta* derivative has a very pale colour. One can understand this by considering the existence of an *ortho*- and *para*-“quinonic” resonance form, that cannot exist in the *meta* derivative.

*Ortho*-nitroaniline (Fig. 2) does not show any evidence of hydrogen bonding<sup>6</sup> despite the fact that it is an *ortho* derivative, where the hydrogen atom is situated between two electronegative elements. This justifies the polar situation of this molecule and only occurs in the *ortho* and *para* derivatives, accounting for the intense yellow colouration of the  $\pi$ -complex from chloranil and these amines. This is not possible for the *meta* derivative.

The coloured  $\pi$ -complex found in the chromatographic detection of aromatic amines with chloranil results from the respective orbitals interleaving, where the amine acts as a good  $\pi$ -donor, while chloranil as the  $\pi$ -acceptor. Qualitatively we may imagine a “sandwich” type situation for these  $\pi$ -complexes, as follows:



For aniline derivatives, the intensity of interleaving, directly related to the complex colour, is influenced by the effects resulting from the position of the substituents present. Taking aniline as a standard amine, we find that the *meta*-halogen derivatives are paler coloured (yellow) than the *para* (yellowish-brown) ones. For example,



only (9.b) has a brownish colour, while acetanilide (9.a) does not react with chloranil under any of the experimental conditions selected for the colour development studies. This can be explained by imagining the existence of a “dimer” in the compound (9.a), formed by intramolecular hydrogen bonds between amide groups. The existence of the situation as in (8) is not possible in this “dimer” form, and the absence of colour is thus explained. In amino-acetanilide this does not occur, because the  $\pi$ -complex form resembles that obtained in the case of benzidine (brown). The chromatic effect intensity depends on this  $\pi$ -complex and thus is affected by dilution as we observed by studying some UV and visible spectra.

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