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## THIN-LAYER CHROMATOGRAPHY OF NITROARENES ON ALUMINA AND ON SILICA GEL

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### SUMMARY

$R_F$  values are reported for 43 nitro-substituted arenes (in the parent systems benzene, naphthalene, biphenyl, fluorene, and 9-fluorenone) for adsorption on alumina and silica gel in an atmosphere of constant relative humidity. It is proposed that the arene system is adsorbed preferentially flatwise with (where possible) the nitro group(s) coplanar to the aromatic ring(s).

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### INTRODUCTION

In continuation of our efforts to rationalize chromatographic adsorbability of organic compounds in terms of geometric and electronic interactions between the substrate molecule and the adsorbent surface, we have measured the  $R_F$  values of a variety of nitro-substituted aromatic compounds (specifically derivatives of nitrobenzene, 1-nitronaphthalene, biphenyl, 2-nitrofluorene, and 9-fluorenone) by means of thin-layer chromatography (TLC) on alumina and silica gel. In order to obtain closely reproducible  $R_F$  values it was necessary to conduct these experiments under conditions of constant temperature and (especially) constant relative humidity, in the manner previously employed for TLC of alkylarenes on alumina<sup>1</sup>. Data obtained, generally reproducible to  $\pm 0.02$  in  $R_F$ , are presented in Tables I-V.

### EXPERIMENTAL

The nitro compounds used were available either from commercial sources or from previous studies in our laboratory<sup>2,3</sup>. Pyrex glass plates (20 × 20 cm) were cleaned and coated either with aluminum oxide G as previously described<sup>4</sup> or with E. Merck (Darmstadt, G.F.R.) silica gel G (according to Stahl, containing *ca.* 13% CaSO<sub>4</sub> as binder) in the same manner. These plates were then activated at 230°-260° for 24 h and transferred to a humidity chamber (with relative humidity either *ca.* 10% or 47%), where they were equilibrated and where chromatograms were run in the

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same manner as described earlier<sup>1</sup>. Adsorbate standard solutions in either benzene or chloroform were  $2 \cdot 10^{-2} M$  (or saturated for less soluble solutes). Spots were made from 2- $\mu$ l aliquots for substituted nitrobenzenes (Table I) or from 1- $\mu$ l aliquots for the other adsorbates (Tables II-V).

Fluorenone was run as a reference compound on every plate, developed with benzene as eluent at room temperature (27-30.5°). The  $R_F$  of fluorenone (no. 38, Table V) (0.39 for alumina at 10% relative humidity; 0.18 and 0.27 for silica gel at 10% and 47% relative humidities, respectively) was used to standardize data for all adsorbates and all plates to the same scale<sup>1</sup>. Thus, all  $R_F$  values in Tables I-V are directly comparable. Spots were detected by spraying the developed plates with an aqueous solution ( $2.5 \cdot 10^{-4} M$ ) of Rhodamine B and then observation in ultraviolet light<sup>1</sup>.

## RESULTS AND DISCUSSION

Comparison of data in Tables I-V shows that orders of adsorbability on alumina and silica gel are closely similar, though not identical. Separability (as measured by the range of  $R_F$  values in each table) is greater on alumina than on silica gel under the same external conditions.

Observation of Table I shows the following trends. Adsorbability increases with substitution of a second nitro group onto the benzene ring. For silica gel, the position of this nitro group has little effect on the  $R_F$  values; while, for alumina, adsorbability is dependent on the position of substitution, in the order 2->3->4-. Adsorbability is enhanced markedly by the presence of a methoxy group. The presence of a methyl group in a position *meta* or *para* to a nitro group either increases adsorbability slightly or shows little effect thereon; while a methyl group *ortho* to a nitro substituent decreases adsorbability. These trends are consistent with an adsorption model wherein the benzene ring is held preferentially flatwise onto the adsorbent

TABLE I

### $R_F$ VALUES FOR SOME SUBSTITUTED NITROBENZENES

For  $28.3^\circ \pm 1.3^\circ$ , 10% relative humidity and benzene as eluent.

No.	Substituent(s) on nitrobenzene	Adsorbent	
		Alumina	Silica gel
1	2,6-diMe	0.76	0.51
2	2,4,6-triMe	0.75	0.51
3	4-NO <sub>2</sub> -2,3,5,6-tetraMe	0.75	0.50
4	2-Me	0.70	0.46
5	2,3-diMe	0.69	0.47
6	3-Me	0.67	0.44
7	4-Me	0.63	0.42
8	3,4-diMe	0.62	0.42
9	3-NO <sub>2</sub> -2Me	0.60	0.40
10	4-NO <sub>2</sub>	0.53	0.36
11	3-NO <sub>2</sub> -4-Me	0.50	0.33
12	3-NO <sub>2</sub>	0.49	0.32
13	4-MeO	0.48	0.28
14	2-NO <sub>2</sub>	0.45	0.34
15	2-MeO	0.42	0.22

surface; as previously proposed for nitrobenzene on silica gel (as based on infrared and ultraviolet spectral measurements)<sup>5</sup>; while both nitro and methoxy groups serve as sites of attachment from the substrate molecule<sup>6</sup> to the adsorbent surface. When these anchoring groups are *ortho* to one another (compounds 14 and 15) enhanced adsorbability on alumina may result from simultaneous or alternating attachment of the two groups to the same adsorption site on the adsorbent<sup>4,7a</sup>. On silica gel this *ortho*-effect is not evident for 1,2-dinitrobenzene (14) in our study and is variable in reported studies on 2-nitroanisole<sup>6,7b</sup>.

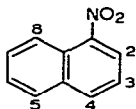
The methyl group assumes the dual roles<sup>4</sup> of enhancing adsorbability slightly (if at all) through the inductive effect and decreasing adsorbability, to a far greater extent, by means of steric hindrance when the group is situated *ortho* to the nitro function. This steric hindrance causes twisting of the nitro group away from coplanarity with the benzene ring<sup>8,9</sup> and interferes both with the close approach of the ring to the surface and with bonding of the nitro group to the adsorbent. The increased extent of this twisting is evident in the higher  $R_F$  values observed for compound 1 (nitro group flanked on both sides by methyl groups) than for compound 4 (only one *ortho* methyl group). The order (in  $R_F$ ) of  $9 > 11$  is consistent with the twisting of both nitro groups in the former compound, but of only one in the latter. Also comparison of 1 and 3 shows that adding a second strongly twisted nitro group to the molecule has virtually no effect on adsorbability. It should be noted that twisting decreases or eliminates conjugation of the nitro group with the benzene ring, *i.e.* it decreases the magnitude of the negative charge which resides on the oxygen atoms.

Similar relationships are apparent in Table II, where (except for the 3-substituent in 22) only  $\alpha$ -nitro groups on the naphthalene ring are considered.  $\alpha$ -Nitro groups are all twisted out of coplanarity with the aromatic ring, even in the parent compound 1-nitronaphthalene (17)<sup>2,10</sup>. Further twisting should occur in 16 (larger  $R_F$  value) due to the methyl group at C-2 and in compounds 20–22<sup>11</sup> (*peri* interaction<sup>12</sup>). Introduction of a second nitro group into a non-*peri* position increases adsorbability slightly (*cf.* 18 and 19 with 17), while introduction of the group into a *peri* position in-

TABLE II

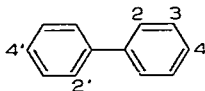
 $R_F$  VALUES FOR SOME SUBSTITUTED 1-NITRONAPHTHALENES

For  $28.3^\circ \pm 1.3^\circ$ , 10% relative humidity and benzene as eluent.



No.	Substituent(s) on 1-nitronaphthalene	Adsorbent	
		Alumina	Silica gel
16	2-Me	0.72	0.54
17	None	0.63	0.48
18	4-NO <sub>2</sub>	0.59	0.47
19	5-NO <sub>2</sub>	0.55	0.42
20	4,5-diNO <sub>2</sub>	0.26	0.33
21	8-NO <sub>2</sub>	0.19	0.22
22	3,8-diNO <sub>2</sub>	0.13	0.20

TABLE III

 $R_F$  VALUES FOR SOME NITROBIPHENYLSFor  $29^\circ \pm 0.5^\circ$ , 10% relative humidity and benzene as eluent.

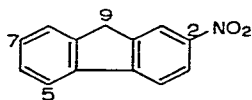
No.	Position(s) of nitro group(s)	Adsorbent	
		Alumina	Silica gel
23	3	0.67	0.49
24	2	0.66	0.48
25	4	0.62	0.47
26	2,2'	0.51	0.37
27	2,4'	0.39	0.33
28	4,4'	0.31	0.30

creases adsorbability considerably more (*cf.* 17 with 21; 18 and 19 with 20) which is in analogy to the *ortho* effect for anchoring groups<sup>7a</sup>.

For nitro-substituted biphenyls (Table III) one notes that substituents at positions *para* to the pivotal bond increase adsorbability more than do those *ortho* or *meta* to this bond. While biphenyl is non-coplanar in solution<sup>7c,13</sup>, an *ortho* nitro group will introduce additional interference with the attainment of coplanarity in the molecule. A *meta* nitro substituent cannot be conjugated with the other ring, while a *para* nitro group can be conjugated and yet not introduce additional interference with coplanarity over that present in biphenyl itself.

An alkyl substituent at C-9 of 2-nitrofluorene will interfere sterically with flat-wise adsorption of the fluorene ring since the alkyl group will protrude sidewise from

TABLE IV

 $R_F$  VALUES FOR SOME SUBSTITUTED 2-NITROFLUORENESFor  $30^\circ \pm 0.5^\circ$  on alumina,  $25^\circ \pm 1^\circ$  on silica gel; 10% relative humidity; benzene as eluent.

No.	Substituent(s) on 2-nitrofluorene	Adsorbent	
		Alumina	Silica gel
29	9-isoPr	0.62	0.48
30	9-Et	0.60	0.46
31	9-Me	0.58	0.44
32	None	0.53	0.43
33	9-NO <sub>2</sub> -9- <i>n</i> -Pr	0.41	0.36
34	9-NO <sub>2</sub> -9-Me	0.36	0.32
35	5-NO <sub>2</sub>	0.32	0.31
36	7-NO <sub>2</sub> -9-Me	0.30	0.30
37	7-NO <sub>2</sub>	0.21	

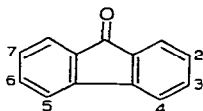
the plane of the ring. Thus, in Table IV, one sees the orders in  $R_F$  of  $29 > 30 > 31 > 32$ ,  $33 > 34$  and  $36 > 37$ , as expected on the basis of the decreasing sizes of the 9-alkyl substituents present. Once again a second nitro group in the molecule increases adsorbability. The second nitro group is considerably more effective in enhancing adsorbability when it occupies the 7-position (where the substituent can be coplanar with the ring) than when it occupies the 5-position (steric hindrance, from the hydrogen atom at C-4, to the attainment of coplanarity) (*cf.* 35 and 37).

Comparison of  $R_F$  values for 2-nitrofluorene (32) and 9-fluorenone (38, Table V) shows that the carbonyl group anchors the molecule more strongly than the nitro group does to either alumina or silica gel. This difference in group adsorption energies was noted by Snyder<sup>7a</sup>. In fact, on silica gel the order of adsorbability  $38 > 32$  holds even though a more active adsorbent (atmosphere of 10% relative humidity) was used for 32 than for 38 (atmosphere of 47% relative humidity). For alumina as an adsorbent one sees clearly from Table V that substituting a nitro group in a sterically unhindered (to coplanarity) 2-, 3-, 6-, or 7-position increases adsorbability appreciably, while substituting a nitro group in a sterically hindered 4- or 5-position has relatively little effect. On silica gel the twisted 4- and 5- nitro substituents decrease adsorbability noticeably. Apparently both the keto group and sterically unhindered nitro substituents serve as anchoring groups for flatwise adsorption of the fluorenone molecule.

TABLE V

 $R_F$  VALUES FOR SOME NITRO-9-FLUORENONES

For benzene as eluent.



No.	Position(s) of nitro group(s)	Adsorbent	
		Alumina ( $30^\circ \pm 0.5^\circ$ , 10% rel. humidity)	Silica gel ( $25^\circ \pm 1^\circ$ , 47% rel. humidity)
38	None	0.39	0.27
39	3	0.34	0.28
40	2	0.18	0.22
41	2,6	0.11	0.21
42	2,4,7	0.08	0.25
43	2,7	0.06	0.13
44	2,4,5,7	0.02	0.22

## CONCLUSIONS

Nitro-substituted benzenes, fluorenes, and 9-fluorenone are adsorbed onto alumina and silica gel preferentially in a flatwise manner with the nitro group coplanar with the aromatic ring. In cases where the nitro substituent is twisted out of coplanarity with the aromatic ring (*e.g.* in *ortho* methyl nitroarenes, in  $\alpha$ -nitronaphthalenes, and in 4- or 5-nitrofluorenes and -fluorenone) flatwise (or nearly flatwise) adsorption of the ring may still occur but adsorbability is less than where the nitro and arene por-

tions are coplanar. In nitrobiphenyls adsorbability increases with increasing facility to the attainment of a completely flatwise conjugated molecule. *peri*-Dinitronaphthalenes exhibit cooperative, enhanced adsorbability.

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