

THE DISCOVERY OF "ORDERING EFFECT" IN META-ISOMER, THE PRODUCT OF BENZENE MONO-DERIVATIVE NITRATION AND RELATION BETWEEN THIS EFFECT AND REACTIVITY OF MONOSUBSTITUTED BENZENES IN THE REACTIONS OF INTERMOLECULAR DONOR-ACCEPTOR INTERACTION WITH C₆₀ FULLERENE

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Introduction

The mesomeric effect discovered at the first half of the past century, and the processes related to this effect are still the subjects of investigation. The mesomeric effect (\pm M-effect) plays an important role in the reactions of intermolecular donor-acceptor interaction, giving rise to the π -complexes, and in the reactions of electrophilic substitution, a classical example of which is a mono-nitration reaction of benzene mono-derivatives. This reaction is of special interest because nitro-isomers qualitative composition in the reaction product reflects the reaction state of carbon atoms in a benzene ring; this state is dependent on substituent electron effects.

Results and discussion

Analysis based on the experimental values of fullerene C₆₀ solubility [1-3] has shown that C₆₀ solubility in the benzene mono-derivatives depends on the substituent nature. Therefore, considering the process of C₆₀ dissolution in respect to the donor-acceptor interactions, it was logical to suppose the functional relationship existing between C₆₀ solubility in benzene derivatives and nitro-isomer concentrations in the product of their mono-nitration reactions.

It has been found that the inverse relationship between C₆₀ solubility and *meta*-nitro-isomer concentration is observed in each homological row only in the case of *meta*-nitro-isomers regardless of the substituent nature. For *ortho*- and *para*-isomers, this relationship can be directly or inversely proportional depending on the substituent nature. A special effect of *meta*-isomers has been also found, it can be named the *ordering effect*. This effect lies in the fact that location of benzene mono-derivatives in the order of increasing *meta*-nitro-isomer concentration in the nitration product creates an original "table of mono-substituted benzenes" in which each compound takes its strict place.

As can be seen from the Table 1, the mono-substituted benzenes under study are distributed in homological rows: the row of halogens – compounds 1,2,3,4; the row of alkyl-benzenes – compounds 6,7,8,9; the following compounds: 10 row – benzyl chloride, 11 row – benzal chloride, 12 row – benzotrichloride, according to the distribution of nitro-isomer concentrations, belong to the same homological row. Benzene derivatives with electron acceptor substituents, compounds 14,15,16,17, also form a homological row.

By its isomers composition, the compound 7 is closer to the row of benzene halides than to the alkyl benzenes although it is closer to the alkyl benzenes by its atomic composition.

The increase in *meta*-isomers concentration, the decrease in +M-effects and fullerene C₆₀ solubility in benzene halides is observed in the row of benzene halides F, Cl, Br, J. The values of fluorine mesomeric effect and C₆₀ solubility in fluorine benzene fall out from the linear relationships existing between these parameters.

For the row of alkyl benzenes, there exists the inverse relationship between *meta*-isomers concentrations and C₆₀ solubility in alkyl benzenes similarly to the row of benzene halides.

In the row of compounds 14,15,16,17, a negative mesomeric effect of substituents enhances in proportion to the increasing *meta*-isomers concentrations. From the physical meaning of the mesomeric effect, this order can be interpreted as the increase in a positive mesomeric effect inversely to the *meta*-isomers concentrations.

According to the current concepts about the mesomeric effect, its influence does not extend on the carbon atoms located in the *meta*-positions. Moreover, there exists almost generally accepted statement that a negative charge is localized on the halogen substituents of benzene.

Table 1. The compositions of nitro-isomers in product of nitration of derivative benzene, mesomeric effects of substituents, fullerene C₆₀ solubility.

No	Substituents	Isomers concentration, %			±M-effect, D	C ₆₀ solubility, mg·ml ⁻¹
		<i>ortho</i> -	<i>meta</i> -	<i>para</i> -		
1.	F	12.4	0.0	87.6	+0.35	1.2
2.	Cl	29.6	0.9	69.5	+0.32	5.7
3.	Br	36.5	1.2	62.3	+0.28	3.3
4.	I	37.9	2.1	60.0	+0.20	2.1
5.	OCH ₃	44.0	2.0	54.0	+strong	
6.	-CH ₃	58.4	4.4	37.2	+	3.0
7.	CH ₂ CH ₃	45.0	6.5	48.5	+	2.16
8.	CH(CH ₃) ₂	30.0	7.7	62.3	+	1.2
9.	C(CH ₃) ₃	15.8	11.5	72.7	+	0.9
10.	CH ₂ Cl	32.0	14.0	54.0	+	2.46
11.	CHCl ₂	23.3	33.8	42.9	—	
12.	CCl ₃	6.8	64.5	28.7	—	
13.	COOCH ₃	28.3	68.4	3.3	—	
14.	COOC ₂ H ₅	24.0	72.0	4.0	-0.15	
15.	CHO	19.0	72.0	9.0	-0.22	0.41
16.	C≡N	17.0	81.0	2.0	-0.39	0.41
17.	NO ₂	6.4	93.3	0.3	-0.69	0.80

The effect of *meta*-isomers ordering is not explained from the viewpoint of such concepts. It may be explained assuming that an electron-donor substituent, due to its positive mesomeric effect, has a positive charge rather than negative one. In this case the influence of energy field of a positive charge will extend on adjacent atoms and inhibit their electron-donor ability. The force of energy field action of a positive charge on adjacent atoms in a molecule is directly proportional to the value of a positive charge. The higher positive mesomeric effect of a substituent, the higher positive charge; the charge decreases with distance. In this situation, carbon atoms in the *ortho*- and *meta*-positions will be the most affected and those in the *para*-position will be less affected by the field. In the row of halogens, for example, a fluorine atom exhibits the highest +M-effect and, consequently, its effect appears better in the *meta*-position as a negative charge of the carbon in the *ortho*- and *para*-positions is increased by the action of its positive mesomeric effect which does not extend to the *meta*-position. Therefore the product of fluorinebenzene nitration contains no *meta*-isomers and negligible amounts of *ortho*-isomer. The force field effect in the *para*-position is weakened by the distance, and the substitution reaction mainly proceeds on the carbon in this position. The decrease in the +M-effect of a substituent weakens the inhibiting action of its positive force field. The *ortho*- and *meta*-isomers concentrations in the mononitration product begin to increase; as this takes place, the fraction of

para-isomers decreases and so does their concentration in the reaction product. Application of the proposed approach in the research of electron effects of substituents on reactivity of the compound carrying this substituent allows the interpretation of current problems and statements from the new viewpoint. For example, there is no need to divide substituents into “*ortho*-, *para*- and *meta*-directing” and some other statements.

Conclusions

1. The “ordering effect” in *meta*-isomer has been discovered.
2. Fullerene C₆₀ solubility in substituted benzenes is defined by the value of the substituent +M effect and by π-electron system mobility in the benzene core. In accordance with the concept developed, low fullerene C₆₀ solubility in fluorinebenzene, in spite of a significant +M effect of fluorine, is conditioned by strong inhibiting action of a positive charge on the fluorine. This statement is agreed with the fact that the fluorinebenzene dipole moment is much less than that of even iodine.
3. The suggestion has been made that halide in C(sp₂) - X bond is positively charged.

References

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