AZO-COUPLING OF 4-SUBSTITUTED PHENOLS. INFLUENCE OF METHOXY GROUP ON 3-POSITION OF BENZENE NUCLEUS

J.KULIČ[a], M.TITZ[b] and M.VEČEŘA[a]

[a]*Department of Organic Chemistry, Institute of Chemical Technology, 532 10 Pardubice and*
[b]*Research Institute of Organic Syntheses, 532 18 Pardubice - Rybitví*

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The azo-coupling kinetics of 4-nitrobenzenediazonium resp. 4-sulfobenzenediazonium ions with 4-substituted phenols have been studied in water at 20°C. The influence has been followed of the substituent in 4-position of benzendiazonium ion on its reactivity with 4-methylphenol and 4-methoxyphenol. In all the cases the reactivity of 4-methoxyphenol was ten times (or more) higher than that of 4-methylphenol. The same reactivity order has been found also for the azo--couplings in deuterium oxide and 50% tert-butyl alcohol media. The reactivity difference between 4-methoxyphenol and 4-methylphenol increases with the diazonium ion reactivity. The reactivity indices of 4-methoxyphenol, 4-methylphenol and their anions have been calculated by HMO method. The results of calculations agree with the data obtained from kinetic measurements.

An interesting behaviour of 4-methoxyphenol under the conditions of electrophilic aromatic substitution was observed earlier[1-3]. Diazotized 4-nitroaniline or sulphanilic acid reacts with 4-methoxyphenol faster than with 4-methylphenol, which is contrary to what can be expected from the respective σ_m^+ constants[1]. An enhanced reactivity of 4-methoxyphenol was observed also in the case of bromination in tetrachloromethane[2].

From our previous papers it follows that the anomalous behaviour of 4-ethoxyphenol is not caused by its electrophilic substitution in some other position[1], neither it is caused by the substituent constant σ_m^+ (determined by Brown[4] in 90% acetone) being changed with polarity of medium[5]. The aim of the present paper was a more detailed kinetic study of azo-coupling of 4-methylphenol and 4-methoxyphenol under various experimental conditions with particular respect to the influence of diazonium ion of anomalous reactivity. The study was extended to some phenols with alkoxy groups in 4-position. The respective pK_a values were determined under the same conditions as those used for azo-coupling kinetic measurements, so that an eventual distortion of results by pK_a's of the phenols might be avoided. The experimental reactivities of 4-methoxyphenol and 4-methylphenol were compared with the reactivity indices obtained by HMO calculations.

EXPERIMENTAL

Reagents. Organic substances were purified by crystallization or distillation before use; their purity was checked by melting points, paper chromatography or gas–liquid chromatography. 4-Nitroaniline, 4-chloroaniline, 4-methylphenol, 4-tert-butylphenol, 4-chlorophenol, sulphanilic acid and 4-hydroxynaphthalene-1-sulphonic acid were commercial reagents. Further substances were prepared by known methods: 4-methoxyphenol (m.p. 54—55°C; ref.[6] 56°C) from hydroquinone[6], 4-ethoxyphenol (m.p. 65°C; ref.[7] 65—66°C) from hydroquinone[8], 4-benzyloxyphenol (m.p. 120—121°C; ref.[7] 121°C) from hydroquinone[7], 4-phenoxyphenol (m.p. 82°C; ref.[7] 83°C) from 4-phenoxyaniline which (m.p. 93°C; ref.[9] 95°C) was obtained from 4-nitrodiphenylether by reduction[9]; the latter substance was prepared from 4-nitrochlorobenzene and potassium phenolate. 4-tert-Butyloxyphenol was obtained by alkylation of 0·1 mol hydroquinone with 0·4 mol butyl chloride in 80% aqueous ethanol in the presence of 0·1 mol sodium hydroxide; yield about 5%, m.p. 150—155°C (crystallization from light petroleum). The purity was checked by GLC and the identity was verified by NMR spectroscopy.

Ionization constants. The p*K*a values were determined spectrophotometrically[10,11]. The measurements were carried out in water at 20°C at the ionic strength 0·3 adjusted by addition of potassium chloride. Mixtures of disodium hydrogen phosphate and trisodium phosphate were used as buffers[11]. The concentrations of phenols for p*K*a determination were chosen about 10^{-4} mol/l. Spectra of the ionized and non-ionized forms and those of their mixtures at pH close to the expected p*K*a were measured with the use of a Unicam SP 800 spectrophotometer. The proper extinction measurements of the samples at seven various pH values (E) and in two various sodium hydroxide (E_I) resp. hydrochloric acid concentrations (E_N) were carried out with a VSU-2P spectrophotometer (Zeiss, Jena) at suitable wavelengths. The pH values were measured with a PHM-4 apparatus (Radiometer, Copenhagen). The pK_a values were calculated from the equation $pK_a = pH + \log((E_I - E)/(E - E_N))$. In the same way the pK_a values of 4-methylphenol and 4-methoxyphenol were measured in 50% aqueous tert-butyl alcohol.

Azo-coupling kinetic measurements. The diazonium salts were prepared by dissolving the respective amine in 2·5 equivalents of hydrochloric acid, cooling and addition of 1·1 eqivalents of 0·1 M-$NaNO_2$. The excess of nitrite was removed by addition of sulphamic acid. The required concentrations were obtained by dilution with cold water. Spectral measurements were used for the azo-coupling kinetic measurements: in cases of soluble products the extinction increases of the dyestuff formed were followed, whereas in cases of insoluble products the decreases of diazonium salt concentration were followed by coupling of the yet unreacted diazonium salt with a reactive coupling component giving soluble azo compounds absorbing at higher wavelengths than the products of the studied reaction. The measurements were carried out at 20°C at the ionic strength 0·3 adjusted by addition of potassium chloride. pH values were measured by means of the PHM-4 apparatus except for solutions having pH < 1, where the titration method was used.

Extinction measurements of dyestuff increases. The increase of extinction of the dyestuff formed was measured with the Unicam SP 800. Its cell contained 10 ml 10^{-3}M phenol in suitable buffer[11], and 0·25 ml $2 \cdot 10^{-3}$M diazonium salt solution was injected thereto at the time t_0. The value E was measured at a time corresponding to about ten reaction half-lives. The experimental rate constant k' was obtained from the equation $k't = 2{\cdot}303 \log(E/(E - E_t)) = \text{const.} - 2{\cdot}303 \log(E - E_t)$. The second-order rate constant k_2 was calculated from the relation $k_2 = k'/[RO^{(-)}] = k'(K_a + [H^+])/K_a[ROH]$, where K_a and [ROH] are the dissociation constant and the analytical concentration of the phenol used, respectively. If $[H^+] \gg K_a$, then the relation is simplified to $k_2 = k'[H^+]/K_a[ROH]$. The decomposition reaction of diazonium salt was followed under the same conditions as those used for azo-coupling rate measurements; the decomposition rate was,

however, negligible as compared to that of azo-coupling. The kinetic study of azo-coupling in 50% tert-butyl alcohol was carried out in the same way.

Measurements of diazonium salt concentrations. 1 ml $2{\cdot}5 \,.\, 10^{-2}$M diazonium salt solution was injected into a stirred 500 ml 10^{-3}M phenol solution (having the ionic strength 0·3 and a suitable pH) at 20°C at the time t_0. At definite time intervals 25 ml samples were withdrawn and added into 50 ml calibrated flasks containing each 10 ml 10^{-1}M 2-hydroxynaphthalene-6-sulphonic acid solution. After 20 minutes 10 ml ethanol was added thereto to remove turbidity and the volume was adjusted with water. The extinctions were measured with the use of the VSU-2P apparatus. The decomposition rate of the diazonium salts was followed in the same way. The experimental rate constant k' was obtained from the equation $k't = 2{\cdot}303 \log (E_0/E_t) = \text{const.} - 2{\cdot}303 \log E_t$, where E_0 is the extinction of the dyestuff at the time t_0.

RESULTS AND DISCUSSION

Dissociation constants of the 4-substituted phenols in water and 50% (by vol.) tert-butyl alcohol are given in Table I.

TABLE I

Rate Constants k' (min^{-1}) and k_2 ($1\ \text{mol}^{-1}\ \text{min}^{-1}$) of Azo-Coupling of 4-Nitrobenzenediazonium Ion with 4-Substituted Phenols at 20°C at Ionic Strength 0·3 and pK_s Values of the Phenols (water, 20°C, ionic strength 0·3)

R	pK_a	pH	$k' \,.\, 10^2$	$k_2 \,.\, 10^{-5}$
CH_3 (*I*)	$10{\cdot}14 \pm 0{\cdot}02$	5·00	1·15	15·9
	$11{\cdot}85 \pm 0{\cdot}22^a$	5·15	1·58	15·4
$(CH_3)_3C$ (*II*)	$10{\cdot}03 \pm 0{\cdot}02$	5·13	1·09	8·7
CH_3O (*III*)	$10{\cdot}12 \pm 0{\cdot}02$	4·00	2·67	354
	$11{\cdot}64 \pm 0{\cdot}03^a$	4·20	4·52	369
C_2H_5O (*IV*)	$10{\cdot}13 \pm 0{\cdot}02$	4·20	4·83	411
$C_6H_5CH_2O$ (*V*)	$10{\cdot}06 \pm 0{\cdot}01$	4·20	2·25	163
C_6H_5O (*VI*)	$9{\cdot}82 \pm 0{\cdot}01$	5·13	1·73	8·4
Cl (*VII*)	$9{\cdot}40 \pm 0{\cdot}03$	6·40	2·67	0·27

[a] In 50% (by vol.) tert-butyl alcohol.

Azo-coupling of the diazotized 4-nitroaniline with the 4-substituted phenols in water. Table I summarizes the results of the measurements. The ratios of the coupling rate constants of 4-nitrobenzenediazonium cation with the 4-substituted phenols to that with 4-methylphenol are: $k_2^{OCH_3}/k_2^{CH_3} \approx 23$, $k_2^{OC_2H_5}/k_2^{CH_3} \approx 27$, $k_2^{OCH_2C_6H_5}/k_2^{CH_3} \approx 10$, $k_2^{OC_6H_5}/k_2^{CH_3} \approx 0{\cdot}5$. If we use the σ_m^+ constants 0·05 and −0·07 for methoxy and

methyl groups[4], respectively, and the reaction constant $\varrho = -3{\cdot}3$ (ref.[12]) for calculation of the coupling rate constants of 4-nitrobenzenediazonium ion with 4-methoxyphenol and 4-methylphenol, we obtain the ratio $k_2^{OCH_3}/k_2^{CH_3}$ about 0·04. From the experimental results it is obvious that alkoxyl groups in 4-position with respect to hydroxyl group activate the position 2 more than the methyl group does, although the reverse should be true according to the substituent constants[13] σ_m^+. The influence of substituents diminishes with their decreasing ability to donate electrons to an electrondeficient system: $CH_3O > C_2H_5O > C_6H_5CH_2O > C_6H_5O$. 4-Phenoxy group already behaves "normally" in accord with its σ_m^+ constant, *i.e.* it deactivates the 2-position so that 4-phenoxyphenol reacts with 4-nitrobenzenediazonium ion more slowly than 4-methylphenol.

Azo-coupling of diazotized sulphanilic acid with 4-substituted phenols in water and deuterium oxide at 20°C. The reaction of 4-sulfobenzenediazonium ion with 4-methoxyphenol is faster than that with 4-methylphenol, too. The same applies for coupling with 4-ethoxyphenol; higher reactivity of 4-alkoxyphenols was found also at 10°C (Table II). The pK_a values of Table I were reduced by 0·15 units (ref.[14,15]) before use for calculation of the coupling rate constants k_2 at 10°C. The reactivity ratios of 4-methoxy- and 4-ethoxyphenols and 4-methylphenol at 20°C are: $k_2^{OCH_3}/k_2^{CH_3} \approx 11$, $k_2^{OC_2H_5}/k_2^{CH_3} \approx 11$; at 10°C is $k_2^{OCH_3}/k_2^{CH_3} \approx 10$. The azo-coupling of 4-sulfobenzenediazonium ion with 4-methoxyphenol in 90% deuterium oxide is

TABLE II

Rate Constants k' (min^{-1}) and k_2 ($l\ mol^{-1}\ min^{-1}$) of Azo-Coupling of Diazotized Sulphanilic Acid with 4-Substituted Phenols in Water at 20 and 10°C at Ionic Strength 0·3 (phenol concentration 10^{-3} mol/l)

R	pH 20°C	k'	$k_2 . 10^{-3}$	pH 10°C	k'	$k_2 . 10^{-3}$
CH_3O	6·84	48·6	936	6·87	15·6	392
	6·84	49·2	965	6·86	13·5	347
	6·83	41·8	808[a]			
C_2H_5O	6·91	53·6	890			
	7·00	68·2	923			
$(CH_3)_3CO$	7·71	31·8	65·3			
	7·70	31·7	66·5			
CH_3	7·59	25·0	88·8	7·53	13·7	39·4[b]
	7·58	22·1	80·3	7·54	12·6	35·4[b]
Cl	8·16	19·1	0·83[c]	8·15	44·7	0·281[c]
	8·11	17·0	0·83[c]	8·00	36·3	0·322[c]

[a] In deuterium oxide. [b] Phenol concentration $2 . 10^{-3}$M, [c] $4 . 10^{-3}$M.

14× faster than that with 4-methylphenol (Table II), *i.e.* the reactivity ratio is practically the same as that found in water. The second-order rate constants k_2 were calculated with the use of the dissociation constants of the phenols measured in water. We presume their change caused by using deuterium oxide instead of water to be negligible.

Azo-coupling of 4-methylphenol and 4-methoxyphenol with various diazonium ions in 50% (by vol.) *tert-butyl alcohol* As lower alcohols (ethanol, methanol) cause considerable decomposition of diazonium salts, we chose tert-butyl alcohol which has not that effect[16], and we used 50% (by vol.) aqueous tert-butyl alcohol. The couplings of 4-methyl- and 4-methoxyphenols were carried out with 4-nitro-, 4-chloro- and 4-sulfobenzenediazonium ions at 20°C at ionic strength 0·3. From the experimental k' values we computed the second-order rate constants k_2 with the use of the p*K*a values of the both phenols measured under the same conditions. The results are given in Table III. 4-Methoxyphenol reacts faster than 4-methylphenol in 50% (by vol.) tert-butyl alcohol, too, the reactivity ratio $k_2^{OCH_3}/k_2^{CH_3}$ being about 21, 16 and 15 for 4-nitro-, 4-chloro- and 4-sulfobenzenediazonium ions, respectively.

Quantum-chemical calculations. The reactivity of individual nuclear positions of the aromatic substrates was studied by the Hückel molecular orbital method (HMO).

TABLE III

Rate Constants k' (min^{-1}) and k_2 ($1\ mol^{-1}\ min^{-1}$) of Azo-Coupling of Benzenediazonium $4\text{-}RC_6H_4N_2^+$ with 4-Methoxyphenol (*III*) ($2 . 10^{-3}$M) and 4-Methylphenol (*I*) ($2 . 10^{-3}$M) in 50% (by vol.) tert-Butyl Alcohol at 20°C at Ionic Strength 0·3

R	*III*			*I*		
	pH	k'	k_2	pH	k'	k_2
H	6·96	16·9	40·5	8·18	18·7	4·38
	6·99	18·7	41·6	8·12	16·1	4·33
Cl	6·39	45·7	407	7·48	21·0	24·8
	6·41	45·7	388	7·50	23·1	25·9
SO_3H	6·16	8·31[a]	25·1	6·80	5·84[a]	1·64
	6·17	8·52[a]	15·1	6·78	5·96[a]	1·75
	6·78	33·1[a]	24·0	—	—	—
	6·78	32·5[a]	23·5	—	—	—
NO_2	5·14	49·5[b]	3 910	4·87	3·75	179
	4·87	50·6[c]	3 730	5·14	8·66	210
	4·04	21·0	4 130	5·51	16·0	175

Concentration of the respective phenol [a] $1 . 10^{-3}$M, [b] $0·4 . 10^{-3}$M, [c] $0·8 . 10^{-3}$M.

The parameters used are given in Table IV. The calculations gave the values of π-electron densities (Q), superdelocalizabilities (S(E)) and π-electron localization energies (A(E)) given in Table V for *ortho*-position (with respect to OH resp. $O^{(-)}$ groups) of phenol, 4-methylphenol, 4-methoxyphenol and their respective anions. Table V gives also the corresponding values for *meta*-position of toluene and anisole. From the Table it follows that dynamic quantum-chemical reactivity indices of electrophilic substitution (S(E) and A(E)) in the *ortho*-position of the aromatic nucleus afford a reactivity prediction agreeing with experimental data, *viz.* that this position of the aromatic nucleus of 4-methoxyphenol (resp. its anion) is more reactive than that of 4-methylphenol (resp. its anion). The prediction obtained from the static index Q for *ortho*-position of the aromatic nucleus agrees with the experiments only in stating a higher reactivity in phenolate, whereas the reactivity ratio of these positions in 4-methoxy- and 4-methylphenols (as well as their anions) is reversed to that observed experimentally. However, this discrepance is not much disturbing, because the value of π-electron density (Q), being a static value, has not such an importance in reactivity predictions as the danymic indices[17,18].

The difference of total π-electron energies between the neutral molecule (resp. its anion) and the corresponding tetrahedral reaction intermediate can form another criterion for reactivity prediction. The intermediates of electrophilic substitution of phenols have presumably the original hydroxyl group (or $O^{(-)}$) changed into carbonyl

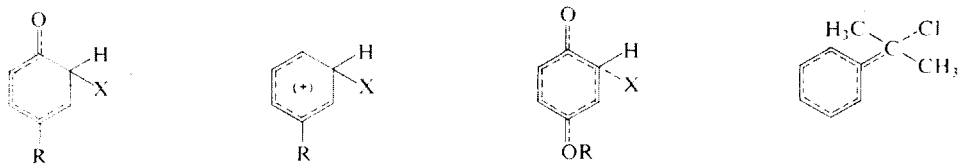
Table IV

The Parameters Used in HMO Calculations

Atomic core (X)	δ_X[a]	Bond (X—Y)	k_{XY}[a]
C^+	0·0	C—C	1·0
O^{+2}	2·0	C—OH	1·0
O^{+2}	2·0	C—O—CH_3	0·8
H_3^{+b}	−0·5	H_3—C	3·0
$C^+(CH_3)^b$	0·0	H_3C—C	0·8
$C^+(—CH_3)$	−0·1	C—CH_3	0·8
$(O^-)^{+2,c}$	1·4	C—O^-	1·0
O^+	1·0	C=O	1·0

[a] Values δ_X and k_{XY} are characteristic constants in expressions for effective coulombic and resonance integrals $\alpha_X = \alpha + \delta_X\beta$, $\beta_{XY} = k_{XY}\beta$. [b] The hyperconjugation model was used for CH_3 group. [c] The value 1·4 for δ of the phenolate oxygen was obtained on the basis of a parameter study carried out by us. Splitting off of the proton giving phenolate oxygen concerns only the σ skeleton and, hence, also this oxygen contributes two π-electrons into conjugation.

group, and the *ortho*-standing carbon atom is supposed to be excluded from conjugation (A); structure B represents an intermediate of electrophilic substitution of toluene and anisole in their *meta*-positions. The total π-electron energies (in β units) of neutral molecules, their anions and the corresponding intermediates are given also in Table V.



A *B* *C* *D*

R = CH_3, OCH_3
X^+ = electrophilic reagent

From the differences of the total π-electron energies it is obvious that the phenolates are more reactive than the corresponding phenols, which stands in accord with the prediction obtained on the basis of all three abovementioned reactivity indices and with experiments. Smaller values of both the differences $(W - W_I)$ and $(W_A - W_I)$ indicate a higher reactivity of 4-methoxyphenol resp. 4-methoxyphenolate anion, which is in accordance with the prediction obtained on the basis of the dynamic reactivity indices S(E) and A(E) and with experimental results.

For the sake of completness and comparison the Table V gives also the values of electrophilic substitution in *meta*-position of aromatic nucleus of anisole and toluene molecules, where the experimental results concerning reactivity of this position give a reverse order as compared with molecules of *p*-substituted phenol or phenolate;

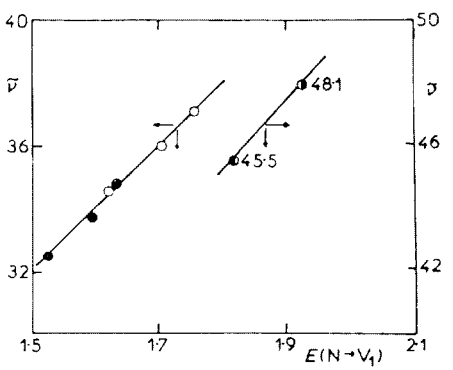


FIG. 1

Correlation between Experimental Frequency $\bar{\nu}(10^3\ cm^{-1})$ of Maximum of the First Intensive Absorption Band and Theoretical Prediction of this Excitation Energy $E(N \rightarrow V_1)$ (in β units)

○ Phenols, ● phenolates, ◑ toluene, ◓ anisole.

as it follows from the given theoretical data this reverse result is confirmed by both the static index Q and dynamic indices $S(E)$ and $A(E)$.

In order to further verify the parameters used by us, we tried to correlate the experimental values of maxima frequencies of the first intensive absorption bands of electronic spectra of all the studied phenols resp. phenolates with the theoretical estimates *i.e.* the values $E(\mathbf{N} \rightarrow \mathbf{V}_1)$ in β units. The respective values are given also in Table V, and the very good correlation can be seen in Fig. 1; this correlation confirms significantly the suitability of the parameters used (Table IV) and increases the weight of the values of quantum-chemical reactivity indices of phenol resp. phenolate *p*-derivatives. As we have compared the studied molecules with only two molecules without OH resp. $O^{(-)}$ group, this correlation cannot be taken as a verification of parameters for toluene and anisole molecules, even though the parameters of CH_3 and OCH_3 groups are, of course, identical for the both sets of compounds. Nevertheless, we suppose that this obvious "breakdown" of the spectral dependence supplements significantly both the experimental and theoretical findings concerning the reverse activating effect of methyl and methoxy groups on the discussed position in the aromatic nucleus of the compounds with and without OH resp. $O^{(-)}$ group; therefore, it can be stated that toluene and anisole represent considerably different

TABLE V

Quantum Chemical Indices of Reactivity in Electrophilic Substitution at *ortho* Position of Aromatic Nucleus of Phenol and its *p*-Derivatives resp. their Anions and at *meta* Position of Toluene and Anisole Molecules

Total π-electron energy of neutral molecules (W), their anions (W_A) and the corresponding intermediates (W_I) (all in β units), frequency values of the first intensive absorption bands of electronic spectra of phenol *p*-derivatives resp. their anions, toluene and anisole ($\bar{\nu}$, 10^3 cm^{-1}) and values $E(N \rightarrow V_1)$ in β units; π-electron density (Q), superdelocalizability $S(E)$ and atomic localization energy $A(E)$ of electrophilic substitution.

Compound	Q	$S(E)$	$A(E)$	W	W_A	W_I	$\bar{\nu}$	$E(N \rightarrow V_1)$
C_6H_5OH	1·0606	1·006	2·313	—	—	—	37·1	1·7551
$C_6H_5O^-$	1·0751	1·098	2·229	—	—	—	34·8	1·6341
III	1·0581	1·019	2·307	22·1283	20·9922	18·1220	34·65	1·6231
I	1·0592	1·011	2·310	17·8763	16·7420	13·8659	36·0	1·7026
$4\text{-}CH_3OC_6H_4O^-$	1·0727	1·122	2·220	—	—	—	32·6[a]	1·5277
$4\text{-}CH_3C_6H_4O^-$	1·0738	1·108	2·225	—	—	—	33·7[a]	1·5914
$C_6H_5CH_3$	0·9989	0·833	2·538	13·5722	—	11·0344	48·1	1·9281
$C_6H_5OCH_3$	0·9980	0·832	2·540	17·8307	—	15·2912	45·5	1·8138

[a] Maxima of the first absorption bands are rather flat and, therefore, the given values are subject to a greater error than those of the other absorption maxima.

molecules as compared with the phenol and phenolate *p*-derivatives studied by us in both the behaviour during electrophilic substitution and behaviour of the first intensive absorption band of electronic spectrum.

CONCLUSIONS

Our experimental results indicate unambiguously increased activation of *m*-position of aromatic nucleus by alkoxy groups (as compared with methyl group) in azo-couplings of phenolate ions. Our former study[2] of bromination showed that the same applies to the electrophilic substitution with bromine in tetrachloromethane where the undissociated phenol is attacked. Quantum-chemical reactivity calculations of the mentioned positions agree with experimental results. The values $-0{\cdot}07$ and $0{\cdot}05$ are given in ref.[4] for σ_m^+ of methyl and methoxy groups, respectively, in aromatic electrophilic substitution. If we accept the substituent constant value of methyl group, then the activating effect of methoxy group in azo-coupling should be expressed, according to our results, by a value $\sigma_m^+ = -0{\cdot}05$.

The activating effect of an alkoxy group in the reaction of phenolate can be represented by the transition state C (X^+ = electrophilic reagent) which shows the delocalization of the electron pair of the alkoxyl oxygen atom. It is probable that the activating effect will make itself felt in the case of attack by weak electrophiles where the bond formation between the electrophile and aromatic carbon is considerably advanced in the transition state.

Formation of the transition state in reaction of a weak electrophile necessitates a strongly activating group (NR_2, $O^{(-)}$) to be present in the aromatic nucleus thus differing from the transtition state *D* of the model reaction (solvolysis of substituted cumyl chlorides) which formed the basis for determination of σ^+ substituent constants. This difference, according to our opinion, is responsible for the different behaviour of *p*-alkoxyphenols and especially their anions in their reactions with weak electrophiles. During electrophilic substitution in *meta*-position of alkoxybenzene the electron delocalization such as in the structure *C* is not significant, and the effect of the alkoxy group on *meta*-position is deactivating. This explanation is very well supported by quantum-chemical calculations.

The study of influence of substituent in diazonium ion on the ratio $k_2^{OCH_3}/k_2^{CH_3}$ of azo-coupling in 50% (by vol.) tert-butyl alcohol shows that the electron-withdrawing substituents increase this ratio: for coupling with *p*-nitrobenzenediazonium ion the ratio $k_2^{OCH_3}/k_2^{CH_3}$ is more than two times greater than that with benzenediazonium ion. Also in aqueous medium the ratio $k_2^{OCH_3}/k_2^{CH_3}$ of azo-coupling of the two phenols with 2,6-dichloro-4-nitrobenzenediazonium ion is three times greater than that of *p*-nitrobenzenediazonium ion. It means that the selectivities of the both reactions (azo-coupling with 4-methyl- and 4-methoxyphenol) are different. So far this observation can merely be stated.

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