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The Reactivity of Aromatic Compounds toward Hydrated Electrons¹BY M. ANBAR² AND EDWIN J. HART

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The specific rates of bimolecular reactions between aromatic compounds and hydrated electrons (e_{aq}^-) have been determined. It has been shown that the reactivity of aromatic compounds toward hydrated electrons is directly related to their reactivity toward nucleophilic reactants as expressed by Hammett's σ -function. The contribution of substituents at different sites on the aromatic nucleus to its reactivity has been analyzed. A mechanism has been suggested for the e_{aq}^- reactions involving the formation of a carbanion as primary product. The hydrated electron may be considered the most elementary nucleophile and by far the most reactive one.

Introduction

The recently discovered hydrated electron that has been identified by its absorption spectrum³ is a unique chemical species consisting of unit negative charge chemically unbound to any particular atom. In its simplicity, this species is unparalleled by any other negative ion. The reaction of the hydrated electron does not involve an atom transfer or sharing of electrons between two species, but must unambiguously be considered as an ideal charge-transfer process. The combination of a hydrated electron with a given molecule requires the incorporation of the electron in one of the molecular orbitals of the reactive substrate. Although extremely reactive toward certain reactants, the hydrated electrons may exist in the presence of other compounds for long periods, which are limited only by the $e_{aq}^- + e_{aq}^-$ and $e_{aq}^- + H$ bimolecular interactions in alkaline methanol solutions. The reactivity of a given compound toward the hydrated electron is evidently determined by the availability of a molecular orbital of sufficiently low energy to interact with the hydrated electron in solution. Following this line of thought, it is evident that the basic chemical properties of a given compound can be examined by a study of its reactivity with e_{aq}^- . Further information on a class of compounds may be gained when certain parameters can be changed at will, as by substitution of one atom by another atom or group. Benzene and its derivatives provide a chemical system in which reactivity is substantially changed by substitution. A study of the aromatic system lends itself as a model to illustrate the potentialities of rate studies of e_{aq}^- reactions. It was, therefore, decided to study the chemical behavior of aromatic compounds from the standpoint of their reactivity with e_{aq}^- .

In previous studies⁴⁻⁶ it has been shown that aromatic compounds react with hydrated electrons at rates which strongly depend on the substituent on the aromatic nucleus. *meta*-Directing substituents have been found to activate the aromatic compound in its reaction with hydrated electrons,⁶ but the effect of *ortho*-*para*-directing groups remained an open question. Another ambiguous point was whether the hydrated electron

interacts with the aromatic nucleus or with its conjugated substituent.⁶ It is the purpose of the present study to examine a large number of aromatic compounds in order to elucidate the factors involved in the reactivity of aromatic compounds and subsequently to postulate a mechanism for these reactions.

Experimental

The rates of reaction of hydrated electrons with organic compounds in homogeneous deaerated aqueous solutions were measured by pulse radiolysis. The experimental set-up as well as the experimental procedures have been previously described in detail.^{4,5} All rate measurements were carried out in the pH range 10.5-11.5.

The aromatic compounds under study were of highest purity commercially available: benzene, toluene, phenol, fluorobenzene, chlorobenzene, bromobenzene, cyanobenzene, nitrobenzene, benzyl alcohol, *o,m,p*-toluic acid, *o,p*-chlorophenol, *p*-bromophenol, *o,m,p*-hydroxybenzoic acid, *o,m,p*-nitrophenol, *o,m*-dichlorobenzene, and *o,m*-chlorobenzoic acid were Fluka puriss grade. Iodobenzene, benzoic acid, sodium benzenesulfonate, naphthalene, trifluoromethylbenzene, *p*-chlorotoluene, *p*-toluenesulfonic acid, *p*-nitrotoluene, *p*-chlorobenzoic acid, *o,m,p*-fluorophenol, *m*-chlorophenol, *o,m*-bromophenol, *p*-iodophenol, *p*-dichlorobenzene, *o,m,p*-fluorobenzoic acid, and *o*-iodobenzoic acid were Fluka purum grade. *o,m,p*-Iodotoluene, *m,p*-iodobenzoic acid, *p*-aminobenzoic acid, α - and β -naphthol, thiophenol, benzamide, and benzenesulfonamide were Eastman White Label chemicals. *o,m,p*-Cyanophenol, *p*-cyanobenzoic acid, 1- and 2-cyanonaphthalene were Aldrich C.P. chemicals; α - and β -naphthoic acids were Matheson C.P. chemicals. Benzoic acid, *p*-chlorobenzoic acid, *p*-aminobenzoic acid, and *o,m,p*-fluorobenzoic acids were recrystallized from a methanol-water solution. All other materials were used without any further purification.

Stock solutions (1 *M*) of benzene, toluene, fluoro-, chloro-, bromo-, iodo-, cyano-, trifluoromethyl-, and dichlorobenzenes were prepared in redistilled methanol. Aliquots of these solutions were injected into the matrix consisting of an aqueous solution of 0.001 *M* NaOH and 0.001 *M* methanol,⁴ thus scavenging the H^+ and OH produced by the pulse. The methanol concentration in these experiments did not exceed 0.25 *M*. Normally 0.001-0.002 *M* MeOH was used in most of the solutions studied. It was shown that methanol up to 3 *M* in aqueous solution does not affect either the lifetime of e_{aq}^- or its reactivity.

The specific bimolecular rate constants were derived from the first-order rates of disappearance of e_{aq}^- which ranged from 1×10^5 to 3×10^6 sec.⁻¹. These values were corrected for the spontaneous rate of disappearance of e_{aq}^- in the same matrix, which ranged from 2.5 to 3.5×10^4 sec.⁻¹. The errors involved in the determination of the bimolecular rate constants originate from three major sources: A, gravimetric and volumetric errors in the concentrations of the reactants; B, errors involved in derivation of rate constants from the photographic records; C, wrongly estimated rate constants owing to the presence of reactive impurities. The first two sources of error limit the accuracy of the specific rate constants to a standard deviation of $\pm 10\%$. The third source of error is negligible in the case of reactive compounds where $k > 10^8$ *M*⁻¹ sec.⁻¹, but it may cause serious error estimates of bimolecular rate constants for compounds of low reactivity. Low rate constants with $k < 10^7$ *M*⁻¹ sec.⁻¹ therefore show a nonsymmetrical distribution of errors and in ex-

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TABLE I
SPECIFIC RATE CONSTANTS AND RELATIVE RATES OF REACTION OF SUBSTITUTED BENZENES, TOLUENES, AND PHENOLS

Substituent X	C_6H_5X		$p\text{-XC}_6H_4CH_3$		$m\text{-XC}_6H_4OH$	
	$k_{C_6H_5X+e_{aq}^-}$, $M^{-1} \text{ sec.}^{-1}$	$\log \frac{k_{C_6H_5X+e_{aq}^-}}{k_{C_6H_6+e_{aq}^-}}$, η	$k_{XC_6H_4CH_3+e_{aq}^-}$, $M^{-1} \text{ sec.}^{-1}$	$\log \frac{k_{XC_6H_4CH_3+e_{aq}^-}}{k_{C_6H_5CH_3+e_{aq}^-}}$, η	$k_{XC_6H_4OH+e_{aq}^-}$, $M^{-1} \text{ sec.}^{-1}$	$\log \frac{k_{XC_6H_4OH+e_{aq}^-}}{k_{C_6H_5OH+e_{aq}^-}}$, η
H	1.4×10^7	0.00	1.2×10^7	0.00	4×10^6	0.00
CH ₃	1.2×10^7	$-.07 \pm 0.07$
OH	4.0×10^6	$-.54 \pm .20$
F	6.0×10^7	$.63 \pm .08$	2.0×10^8	1.70
Cl	5.0×10^8	$1.55 \pm .05$	4.5×10^8	1.57	5.0×10^8	2.10
Br	4.3×10^9	$2.52 \pm .08$	2.7×10^9	2.83
I	1.2×10^{10}	$2.93 \pm .06$	1.3×10^{10}	3.03
CN	1.6×10^{10}	$3.06 \pm .06$	1.4×10^{10}	3.07	4.8×10^9	3.08
COO ⁻	3.1×10^9	$2.35 \pm .05$	3.6×10^9	2.48	1.06×10^9	2.42
SO ₃ ⁻	4.0×10^9	$2.46 \pm .05$	1.65×10^9	2.14
NO ₂	3.0×10^{10}	$3.33 \pm .05$	1.9×10^{10}	3.22	2.5×10^{10}	3.80
CF ₃	1.8×10^9	$2.11 \pm .05$
CH ₂ OH	1.3×10^8	$0.97 \pm .05$
SH	4.7×10^7	$0.53 \pm .05$
CONH ₂	1.7×10^{10}	$3.08 \pm .05$
SO ₂ NH ₂	1.6×10^{10}	$3.06 \pm .05$

trème cases k may be considered only as an upper limit. All these factors were taken into account in estimating the standard deviations of η -values given in Table I.

Results and Discussion

The specific rate constants of the bimolecular reactions of hydrated electrons, e_{aq}^- , with a series of mono-substituted benzene derivatives are given in Table I. The rate of reaction varies over four orders of magnitude, from $4 \times 10^6 M^{-1} \text{ sec.}^{-1}$ for phenol to $3 \times 10^{10} M^{-1} \text{ sec.}^{-1}$ for nitrobenzene. The specific reaction rates of substituted benzene have been related to that of benzene and expressed in terms of η -values, where $\eta = \log [k_{C_6H_5X+e_{aq}^-}/k_{C_6H_6+e_{aq}^-}]$. Comparable values of η are obtained for substituted toluenes and phenols.

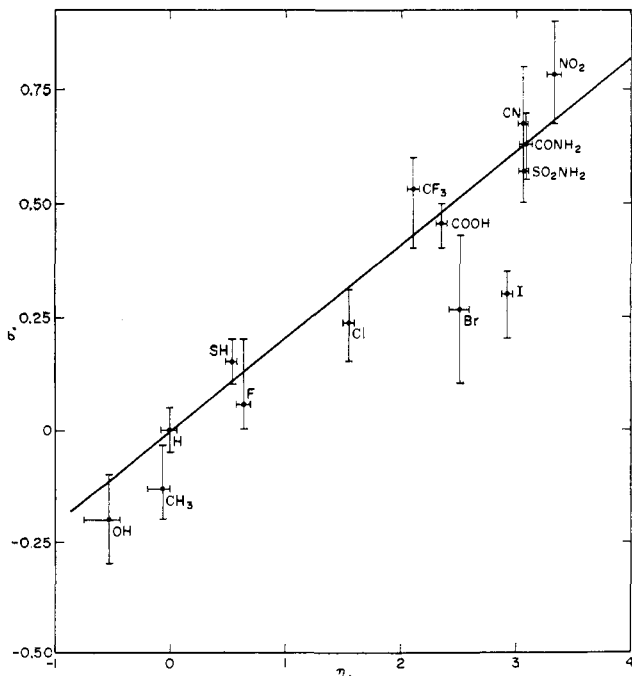


Fig. 1.— η as a function of σ of Hammett's equation.¹⁴
 $\eta = \log [k_{C_6H_5X+e_{aq}^-}/k_{C_6H_6+e_{aq}^-}]$

The η -values which indicate the relative reactivity of an aromatic system carrying a given substituent may be correlated with the effect of the same substituent on

the reactivity of these systems toward nucleophilic or electrophilic reagents. A quantitative evaluation of these effects has been achieved by the use of Hammett's equation, $\log [k_{C_6H_5X}/k_{C_6H_6}] = \rho\sigma$.⁷⁻¹² When the η -values are plotted against the σ_{para} values compiled by Van Bekkum, *et al.*,¹⁰ a satisfactory correlation is obtained for all substituents studied with the exception of bromine and iodine (Fig. 1).

The σ -values of Van Bekkum, *et al.*, are equal within experimental error with the σ_{para} values given by McDaniel and Brown.¹¹ From the η - σ correlation, a ρ -value of 4.8 is obtained, which is within the range of ρ -values obtained for various substitution reactions.¹²

It is evident that the reactivity of aromatic compounds toward e_{aq}^- is determined by the same parameters which control their reactivity toward electrophiles and nucleophiles. As in aromatic bimolecular nucleophilic substitution,¹³ a negatively charged intermediate is formed as the primary product. The formation of carbanions in the reactions of e_{aq}^- with organic molecules has been demonstrated.^{5,14} The lifetime of these carbanions may be limited by their dissociation to a substituted phenyl radical and a stable anion. This pattern of reaction has been demonstrated in the e_{aq}^- induced deiodination of the iodo-benzoic acids, where iodide ions and biphenic acids are formed.¹⁵ Alternatively, the lifetime of these carbanions is determined by the rate of their neutralization by the solvent resulting in the addition of an H^+ .¹⁴

The analogy between e_{aq}^- reactions and nucleophilic aromatic substitution may be of questionable value since our e_{aq}^- rate constants correlate better with "normal" σ -values derived from electrophilic substitution than with *para* σ -values obtained from data of nucleophilic reactions. This is not surprising

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in view of the fact that with e_{aq}^- we are concerned with an interaction of an electron with the π -orbitals of the ring, as in electrophilic substitution, rather than with effects on electron distribution and polarizability of a certain substituent.

The analogy between σ - and η -values has certain limitations. This is found when checking on the additivity of η -values in disubstituted benzenes. A series of *para* derivatives of benzoic acid was examined for their rate of reaction with e_{aq}^- (Table II), and their

TABLE II
SPECIFIC RATE CONSTANTS AND RELATIVE RATES OF REACTIONS OF *para* SUBSTITUTED BENZOIC ACIDS

Substituent	$k_pXC_6H_4COO^-$, $M^{-1} \text{ sec.}^{-1}$	$\log (kXC_6H_4COO^- / kC_6H_5COO^-, \eta)$
H	3.1×10^9	0.00
O ⁻	4.0×10^8	-.89
NH ₂	2.1×10^9	-.17
CH ₃	3.0×10^9	-.01
F	3.8×10^9	.09
Cl	6.0×10^9	.29
Br	7.7×10^9	.40
I	9.1×10^9	.47
CN	1.0×10^{10}	.51
COO ⁻	7.3×10^{9a}	.37

^a Value taken from ref. 6.

η -values, relative to benzoic acid, were calculated. With the exception of the value for OH, these η -values are proportional to the η -values of the benzene series (Fig. 2) and the excellent correlation between these two series yields $6.5\eta_{C_6H_5COOH} = \eta_{C_6H_6}$. Consequently, taking $\eta = \rho\sigma$, one may assign to the benzoic acid series a ρ -value of $4.8/6.5 = 0.74$.

The behavior of the benzoic acid series exhibits a principal difference between the application of Hammett's equation to aromatic substitution and to the e_{aq}^- reactions. In aromatic substitution, the σ -values are additive to a first approximation and ρ is constant for any particular reaction, *e.g.*, nitration, bromination, hydrolysis etc. σ -Values of two substituents become nonadditive when there is an electronic interaction between both. However, as long as such an interaction does not affect the reactive center, σ -values are additive.^{8,12} The η -values, on the other hand, express changes in the over-all probability of incorporation of an additional electron into the molecule as a whole. It is evident that η -values of different substituents are not additive; however, a constant ρ is obtained for any homologous disubstituted series in which one substituent is kept constant and the other is being changed. The higher the rate constant of the nonsubstituted parent compound the lower the η -values of the series. This conclusion is confirmed by the η -values of the phenol series (Table I). A molecule, C_6H_5X , which has a high probability of accepting an electron, will be affected to a smaller extent by an additional substituent. The smaller η -values observed in the more reactive series may also be anticipated in view of the fact that the rate of these reactions approaches the diffusion-controlled limit, $\sim 10^{10} M^{-1} \text{ sec.}^{-1}$, where a further increase in rate cannot occur.

A deeper insight into the mechanism of interaction of a hydrated electron with aromatic molecules may be gained by considering the reciprocal action of two substituents. The relative rates of a series of di-

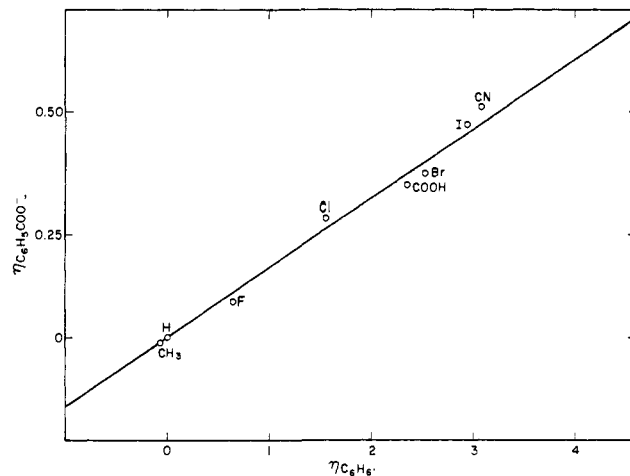


Fig. 2.— $\eta_{C_6H_5COO^-}$ as a function of $\eta_{C_6H_6}$.
 $\eta_{C_6H_5COO^-} = \log [kXC_6H_4COO^- + e_{aq}^- / kC_6H_5COO^- + e_{aq}^-]$
 $\eta_{C_6H_6} = \log [kC_6H_5X + e_{aq}^- / kC_6H_6 + e_{aq}^-]$

substituted benzenes presented in Table III compares the effects of two substituents when in *ortho*, *meta*, or *para* positions to each other. The compounds may be divided into two groups: A, compounds in which the *meta* and *para* derivatives are of comparable reactivity, within experimental error. These include the COO⁻-CH₃, Cl-O⁻, Br-O⁻, NO₂-O⁻, and Cl-Cl couples. B, compounds in which $k_{meta} > k_{para}$: COO⁻-F, COO⁻-I, COO⁻-O⁻, CN-O⁻, and F-O⁻. At first sight it could be suggested that when the two substituents are conjugated in the *para* positions they decrease the probability of a *direct* interaction of e_{aq}^- with them. This is, however, rather unlikely as COO⁻, O⁻, or CN groups show a very small tendency to accept an electron into their orbitals.¹⁶ Aliphatic carboxylic acids, alcohols, as well as acetonitrile, show a low reactivity toward e_{aq}^- . It may be concluded, therefore, that one of the substituents of the second group *increases* the π -electron density of the ring by resonance while it withdraws electrons by induction.

The *meta-para* effect may be explained by the changes in electron density at the different positions on the aromatic ring. This may be illustrated by the examples: Taking fluorophenol, one obtains the following charge distribution for the *meta* and *para* isomers (OH at position 1). Positions 2 and 6 in both isomers are of high electron density owing to the electron-donating power of the OH. Positions 3 and 5 in the *para* isomer are of relatively lower electron density, but in the *meta* isomer position 5 is exceptionally electron deficient and comprises an ideal site for the attack of a nucleophile. Fluorobenzoic acid presents a similar situation. Although COO⁻ is an electron-withdrawing group, it manifests a negative inductive effect on positions 2 and 6 leaving again position 5 of the *meta* isomer as an exceptionally reactive electrophilic center. From this discussion it may be implied that the e_{aq}^- reaction is, at least in part, a highly *localized* attack on the aromatic nucleus and e_{aq}^- may therefore be considered as a reactive nucleophilic species in the classical sense.¹⁷

In view of the conclusion that e_{aq}^- reaction may be rather localized, it is surprising to find such a good

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TABLE III
 THE RELATIVE RATES OF REACTION OF DISUBSTITUTED AROMATIC COMPOUNDS

Substituents		$k_oXC_6H_4Y$, $M^{-1} \text{ sec.}^{-1}$	$k_mXC_6H_4Y$, $M^{-1} \text{ sec.}^{-1}$	$k_pXC_6H_4Y$, $M^{-1} \text{ sec.}^{-1}$	$\log (k_{meta}/k_{para})$	$\log (k_{ortho}/k_{meta})$
X	Y					
COO ⁻	CH ₃	2.7×10^8	2.6×10^9	3.0×10^9	-0.06	-1.03
COO ⁻	F	3.1×10^9	6.7×10^9	3.8×10^9	.25	-0.30
COO ⁻	Cl	1.2×10^9	5.5×10^9	6.0×10^9	-.04	-.66
COO ⁻	I	4.6×10^9	1.3×10^{10}	9.1×10^9	.16	-.93
COO ⁻	O ⁻	3.2×10^9	1.1×10^9	4.0×10^8	.42	.48
F	O ⁻	3.4×10^8	2.0×10^8	1.2×10^8	.22	.23
Cl	O ⁻	2.0×10^8	5.0×10^8	6.4×10^8	-.10	-.40
Br	O ⁻	1.9×10^9	2.7×10^9	2.9×10^9	-.03	-.15
CN	O ⁻	8.2×10^9	4.8×10^9	2.0×10^9	.38	.23
NO ₂	O ⁻	2.0×10^{10}	2.5×10^{10}	2.5×10^{10}	.00	-.10
Cl	Cl	4.7×10^9	5.2×10^9	5.0×10^9	.01	-.04

correlation with σ_{para} values. It is likely that the e_{aq}^- reaction is controlled by the existence of a vacant orbital wherever made available; thus in mono-substituted benzene its reactivity is determined by the over-all π -electron density, whereas in the disubstituted aromatic derivatives the formation of a localized electron-deficient center becomes of greater importance.

Taking the k_{ortho}/k_{meta} ratios, one encounters two groups of disubstituted derivatives: A, $k_{ortho} > k_{meta} > k_{para}$ including COO⁻-O⁻, F-O⁻, CN-O⁻. In these cases the electron-donating capacity of O⁻ appears to be partially neutralized by the neighboring electron-withdrawing groups resulting in a smaller effect on the electron density of the ring. B, $k_{ortho} < k_{meta}$ including all the disubstituted benzenes which shows $k_{para} \approx k_{meta}$. It is suggested that a mutual inductive effect of two electron-withdrawing groups, which is enhanced by the negative charge on one of them, decreases the withdrawal of electrons from the π -orbitals of the aromatic nucleus.¹⁸ Thus we encounter an "ortho effect" which has nothing to do with steric hindrance. This inductive effect manifests itself also in the pK_a values of the corresponding acids and phenols.

The case of iodo and bromo derivatives requires a separate discussion. These compounds show higher η -values than expected from their effects on the electron density of the ring. Comparing iodine and bromine with other substituents for their reactivity with e_{aq}^- in aliphatic systems one finds the iodoaliphatic compounds highly reactive toward e_{aq}^- , unlike cyano, carboxy, fluoro, or even chloro derivatives.^{6,19} In other words, carbon-bound iodine, and to a certain extent bromine and chlorine, are capable of direct interaction with hydrated electrons. In the case of aromatic chlorine this tendency is neutralized by electron withdrawal from the nucleus. Iodine, having a small inductive effect,^{9,18} may retain this property, and an iodo aromatic compound may interact with e_{aq}^- in two fashions—through the nucleus and through the iodine atom. A single product of reaction may still be formed as the negatively charged molecule will achieve its most stable configuration in a very short time compared with its lifetime. The good agreement both for Br and I in the $\eta_{C_6H_5} - \eta_{C_6H_4COOH}$ correlation implies an enhancement also of the "direct" reaction with e_{aq}^- induced by the presence of the carboxylic group. This may be plausible in view of the

enhanced electron withdrawal from the halogen by the HOOC \dot{C}_6H_4 radical compared with \dot{C}_6H_5 . We conclude that a direct interaction with the substituent is likely to contribute to the over-all rate of reaction of aromatic iodine and bromine derivatives.

A number of other aromatic compounds has been examined for their rates of reaction with e_{aq}^- . The results are summarized in Table IV. The naphthalene

 TABLE IV
 SPECIFIC RATE CONSTANTS OF MISCELLANEOUS AROMATIC COMPOUNDS

Compound	$k, M^{-1} \text{ sec.}^{-1}$
1-Naphthol	9.6×10^8
2-Naphthol	1.2×10^9
Naphthalene	5.4×10^9
Naphthalene	5.2×10^{9a}
1-Naphthoate	6.1×10^9
2-Naphthoate	9.5×10^9
1-Cyanonaphthalene	2.13×10^{10}
2-Cyanonaphthalene	2.07×10^{10}
<i>p</i> -NH ₂ C ₆ H ₄ SO ₃ ⁻	4.6×10^8
<i>p</i> -CH ₃ C ₆ H ₄ SO ₃ ⁻	1.65×10^9
C ₆ H ₅ CH ₂ Cl	5.1×10^{9b}
C ₆ H ₅ CH ₂ Cl	5.5×10^{9c}
OHCH ₂ CH ₂ Cl	4.0×10^{9c}
C ₆ H ₅ CCl ₃	8.3×10^{9c}
CHCl ₃	3.0×10^{10d}

^a Value obtained in EtOH.¹⁸ ^b Value obtained in EtOH.
^c Value taken from ref. 20 for comparison. ^d Value taken from ref. 4 for comparison.

derivatives represented in the first group show an analogous behavior to the benzene derivatives (Table I), with OH acting as a deactivating and COO⁻ and CN as activating substituents. It should be noted that naphthalene is much more reactive toward e_{aq}^- than benzene, although it is also more reactive toward electrophiles.¹² This is a result of the reciprocal action between the two rings—whereas one is more nucleophilic than benzene the other is more electrophilic. α -Naphthol and α -naphthoate are less reactive than their β -isomers, a fact probably caused by a stronger interaction with the nonsubstituted ring. In the case of α -naphthol partial deactivation of the non-substituted ring results, whereas in the case of α -naphthoate the electrophilic reaction center becomes more diffuse.

A comparison of the reactivities of *p*-NH₂C₆H₄SO₃⁻ and *p*-CH₃C₆H₄SO₃⁻ demonstrates again the pronounced deactivating power of electron-donating groups.

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The third group of compounds to be considered in Table IV is benzyl chloride and α, α, α -trichlorotoluene. The rate of the $C_6H_5CH_2Cl$ reaction is faster than expected for the CH_2Cl group as an aliphatic substituent, when compared with β -chloroethanol. We conclude, therefore, that the aromatic nucleus is activated toward a nucleophilic attack by electron withdrawal, both by inductive and by resonance effects. The chlorine atom, on the other hand, is also activated by the aromatic nucleus.¹⁹

The interaction of e_{aq}^- with $C_6H_5CCl_3$, on the other hand, is in greater part a *direct* interaction with the chlorine atoms.¹⁹ In fact, this rate is *slower* than that with chloroform.⁴ This is attributed to a withdrawal of electrons from the aromatic nucleus resulting in partial deactivation of the $-CCl_3$ group.¹⁹ This last case is another example of a direct reaction of e_{aq}^- with a substituent. The use of our e_{aq}^- rate constants as a measure of electron density in the nucleus is therefore limited to substituents which do not readily interact directly with e_{aq}^- .

It is interesting to find that comparable rate constants are obtained for the naphthalene and benzyl chloride + e_{sol}^- reactions in water and in ethanol. As the anionic product is a sparingly solvated species, this result corroborates the conclusion that the solvation of the electron in both solvents is comparable.²⁰

In conclusion, it can be stated that the hydrated electron may be considered as the most elementary nucleophile as well as the simplest reducing agent. The rules that apply to the e_{aq}^- reaction are governed by the same parameters that determine aromatic substitution¹³ and the information gained from the e_{aq}^- reactivity may be applied to aromatic chemistry in general. It is gratifying to observe that the Hammett's free-energy relationship holds up to the limit of diffusion-controlled processes.

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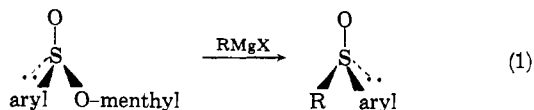
Optically Active Sulfoxides. The Synthesis and Rotatory Dispersion of Some Diaryl Sulfoxides²

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Several optically active diaryl sulfoxides have been prepared by treating optically active (–)-menthyl (–)-arenesulfonates with arylmagnesium bromides. This reaction is shown to produce optically pure sulfoxides. The optical rotatory dispersion curves and ultraviolet spectra of the sulfoxides and the sulfinate esters were determined and are discussed.

Sulfoxides can be synthesized by treating sulfinate esters with Grignard reagents.⁴ If the sulfinate esters are optically active at sulfur, optically active sulfoxides are formed. The first example of the use of this method was reported in a preliminary communication.⁵ (+)-Ethyl *p*-tolyl sulfoxide (2) was prepared by the reaction of (–)-menthyl (–)-*p*-toluenesulfinate (1) with ethylmagnesium iodide.



Since then, the syntheses of several other optically active sulfoxides using this method have been reported.^{6–9} In this paper we wish to report not only

on the synthesis and optical rotatory dispersion (o.r.d.) curves of some diaryl sulfoxides, but also on the mechanism of the reaction used to synthesize them. The diaryl sulfoxides were obtained by treating (–)-menthyl (–)-arenesulfonates with Grignard reagents as in eq. 1. Before discussing the individual sulfoxides, several questions concerning this general reaction should be answered. First, does the reaction proceed with inversion of configuration at sulfur as pictured in eq. (1), with retention, or with some of each? Second, what is the absolute configuration at sulfur?

The chief evidence that inversion takes place at sulfur can be summarized briefly. Phillips¹⁰ demonstrated that alcoholysis of alkyl *p*-toluenesulfinate esters proceeds with inversion. Johnson and Sapp¹¹ reported that alkoxysulfonium salts, $ROSR_2^+$, prepared from optically active sulfoxides are hydrolyzed to sulfoxides of opposite sign of rotation; that is, the hydrolysis proceeds with inversion. Both of these reactions, the alcoholysis and the hydrolysis, proceed

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