

sponding values of p_{a_H} ($\equiv -\log a_{H^+}$) by application of the Bates–Guggenheim¹¹ convention

$$-\log \gamma_{Cl} = Am^{1/2}/(1 + 1.5m^{1/2})$$

The values obtained for the p_{a_H} of one buffer mixture from 0 to 50° are given in Table IV.

(11) R. G. Bates and E. A. Guggenheim, *Pure Appl. Chem.*, **1**, 163 (1960).

The γ Radiolysis of Liquid 2-Propanol. II.^{1a} The Reaction of Solvated Electrons with Mono- and Disubstituted Benzenes

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The effect of a number of mono- and disubstituted benzenes on the gaseous products of the radiolysis of solutions of nitrous oxide in 2-propanol has been studied. The substituted benzenes decrease the nitrogen yield, and this is interpreted as being due to competition with nitrous oxide for solvated electrons. From the measurements of $G(N_2)$ the relative reactivities of the substituted benzenes have been calculated. The site of attack of the solvated electron appears to be the aromatic ring since the substituent effects correlate well with those found generally in aromatic bimolecular nucleophilic substitution. In addition, satisfactory correlation is observed between reactivity and the Hammett σ_{para} functions. The ρ value for the monosubstituted benzenes is 3.1. The ρ value remains approximately constant for a given series of disubstituted benzenes in which one substituent is kept unchanged. However, the σ values for disubstituted benzenes are not additive.

Introduction

Solvated electrons are produced in the radiolysis of aliphatic alcohols.² A knowledge of the subsequent reactions of this species is necessary for the complete understanding of the radiation chemistry of alcohols and alcoholic solutions. It has been shown^{1a} that the molecular nitrogen produced in the radiolysis of dilute solutions of nitrous oxide in 2-propanol is a convenient measure of the solvated electrons which are amenable to solute scavenging. Utilizing this technique, the measurement of the relative rate constants of a number of mono- and disubstituted benzenes are reported.

Experimental Section

Materials. 2-Propanol was purified as described previously.^{1a} The mono- and disubstituted benzenes

were of reagent grade and used without further purification.

Procedure. The preparation and irradiation of the samples, and the analysis of gaseous products were as described previously.^{1a} The mean dose rate during the course of the present series of experiments was 3.7×10^{17} ev ml⁻¹ min⁻¹. All solutions were irradiated for 15 min.

(1) (a) Part I: W. V. Sherman, *J. Phys. Chem.*, **70**, 667 (1966). A preliminary communication of some of the results reported here appears in W. V. Sherman, *J. Am. Chem. Soc.*, **88**, 1567 (1966). (b) The Radiation Laboratory, University of Notre Dame, Notre Dame, Ind.

(2) M. C. Sauer, S. Arai, and L. M. Dorfman, *J. Chem. Phys.*, **42**, 708 (1965), and references therein.

Table I: γ Radiolysis of 2-Propanol Solutions of Nitrous Oxide and a Substituted Benzene

Substituted benzene, mM		Nitrous oxide, mM	$G(\text{H}_2)$	$G(\text{CH}_4)$	$G(\text{N}_2)$	$k_{\text{N}_2\text{O}}$
None	...	5.0	3.37 ^a	1.36 ^a	1.70 ^a	...
None	...	10	3.25 ^a	1.36 ^a	2.06 ^a	...
None	...	50	3.18 ^a	1.36 ^a	2.70 ^a	...
1 Phenol	500	5.0	3.52	1.10	0.83	0.010
2 Toluene	500	5.0	2.11	1.06	0.70	0.014
3 Benzene	0.021 ^a
4 Fluorobenzene	100	10	2.86	1.05	1.37	0.050
5 Chlorobenzene	50	50	2.78	1.30	1.76	0.54
6 Bromobenzene	50	50	2.46	1.16	1.32	1.0
7 Iodobenzene	50	50	2.12	1.38	1.09	1.5
8 Benzaldehyde	50	50	2.78	1.37	1.09	1.5
9 Benzoic acid	50	50	2.68	1.29	1.37	0.97
10 Benzophenone	50	50	2.12	1.47	1.17	1.3
11 Acetophenone	50	50	2.63	1.41	1.00	1.7
12 Benzonitrile	50	50	2.48	1.27	0.93	1.9
13 Nitrobenzene	2.3 ^a
14 <i>p</i> -Chlorophenol	50	50	2.78	1.38	1.98	0.36
15 <i>p</i> -Bromophenol	50	50	3.03	0.61	1.41	0.92
16 <i>p</i> -Hydroxybenzoic acid	50	50	3.05	0.64	1.66	0.63
17 <i>p</i> -Hydroxyacetophenone	50	50	2.81	0.90	1.56	0.73
18 <i>p</i> -Hydroxybenzonitrile	50	50	2.80	0.66	1.14	1.4
19 <i>p</i> -Hydroxynitrobenzene	50	50	2.82	0.43	0.93	1.9
20 <i>p</i> -Chlorotoluene	50	50	2.42	1.50	1.82	0.48
21 <i>p</i> -Dichlorobenzene	50	50	2.50	1.21	1.15	1.3
22 <i>p</i> -Bromochlorobenzene	50	50	2.43	1.29	1.02	1.6
23 <i>p</i> -Chloriodobenzene	50	50	2.58	1.49	0.77	2.5
24 <i>p</i> -Chlorobenzoic acid	50	50	2.25	1.25	1.13	1.4
25 <i>p</i> -Chlorobenzonitrile	50	50	2.62	1.39	0.92	1.9
26 <i>p</i> -Chloronitrobenzene	50	50	2.56	1.23	0.79	2.4
27 <i>m</i> -Dinitrobenzene	50	50	2.43	1.09	0.68	3.0

^a Taken from ref 1a.

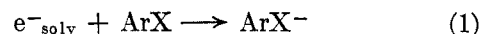
Results and Discussion

The yields of gaseous products from the radiolysis of solutions of 2-propanol containing nitrous oxide and a substituted benzene are listed in Table I. In all cases hydrogen, nitrogen, and methane were the sole products volatile at liquid-air temperature. Qualitatively, all the aromatic compounds studied decreased the hydrogen and nitrogen yields below those observed from 2-propanol solutions containing nitrous oxide alone. The yield of methane appears to be relatively insensitive to the addition of the aromatic compounds except those containing the hydroxy group where a distinct decrease in $G(\text{CH}_4)$ may be observed.

The decrease in $G(\text{N}_2)$ observed in the presence of the substituted benzenes may be taken to indicate competition with nitrous oxide for the solvated electron.^{1a} The reactivities of the substituted benzenes relative to nitrous oxide, $k_{\text{N}_2\text{O}}$, may be calculated from expression A^{1a} and are listed in the last column of Table I.

$$k_{\text{N}_2\text{O}} = \frac{\Delta G(\text{N}_2)}{G(\text{N}_2)} \frac{(\text{N}_2\text{O})}{(\text{ArX})} \quad (\text{A})$$

The solvated electron is a strongly nucleophilic species. Its reactions with aromatic compounds may be expected to conform to the general pattern of bimolecular nucleophilic substitution, $\text{S}_{\text{N}}2$, if the insertion of the solvated electron into the aromatic ring is the rate-determining step of the electron-capture process 1.



The modified Hammett equation, $\log k_{\text{C}_6\text{H}_6} = \rho^- \sigma^-$, where $k_{\text{C}_6\text{H}_6}$ is the rate of the substituted benzene relative to benzene, has been used to correlate the substituent effect in the reactions of a number of nucleophilic species (*e.g.*, CH_3O^- , N_3^- , SCN^-) with substituted benzenes.^{3,4} In Figure 1 the logarithm of the

(3) P. R. Wells, *Chem. Rev.*, **63**, 191 (1963).(4) J. Miller, A. J. Parker, and B. A. Bolto, *J. Am. Chem. Soc.*, **79**, 93 (1957).

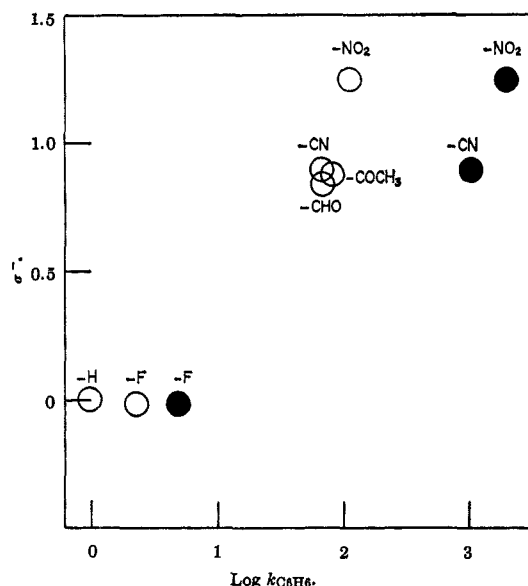


Figure 1. Plot of σ^- functions^{3,4} for nucleophilic substitution vs. $\log k_{\text{C}_6\text{H}_6}$ values for the electron in 2-propanol (O) and water⁵ (●).

rate constants relative to that of benzene for several monosubstituted benzenes is plotted against the substituent constants, σ^- , for $\text{S}_\text{N}2$ reactions on the ring. A "best straight line" does not pass through the point for benzene, and this may indicate that there is a contribution to the observed reactivity from the direct interaction between the solvated electron and the substituent. The ρ^- value (ca. 2) corresponding to the slope of "best straight line" is somewhat lower than those observed with other nucleophiles (3.1 to 9.2).⁴ This low sensitivity to substituent effects probably reflects the high intrinsic reactivity of the solvated electron toward aromatic substrates. In their study of the reactivity of substituted benzenes toward hydrated electrons, Anbar and Hart⁵ noted that the correlation between reaction rates and σ^- values was less than satisfactory in three cases where the reactivity of the aromatic compound toward nucleophilic substitution is known. The data on the hydrated electron are included in Figure 1 for comparison with the present data.

In Figure 2 the values of $\log k_{\text{C}_6\text{H}_6}$ for the monosubstituted benzenes are plotted against the corresponding rate constants for the reaction of the hydrated electron with monosubstituted benzenes.⁵ A good linear correlation may be noted. The slope differs from unity, and it may be concluded that the reactions of the solvated electron in 2-propanol are less sensitive to substituent effects than the equivalent reactions of the solvated electron in water.

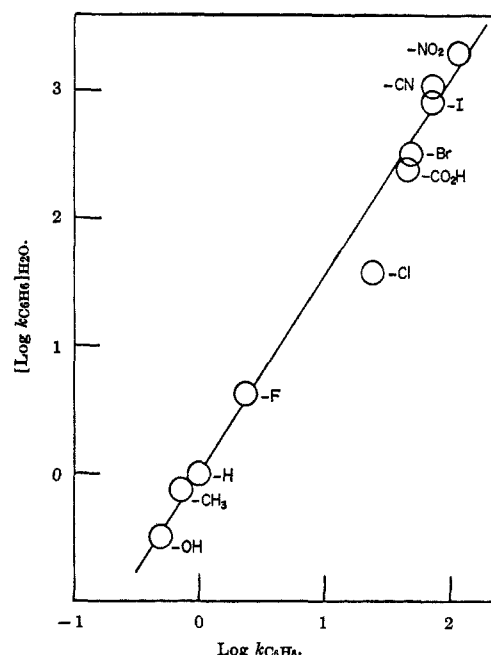


Figure 2. Plot of $\log k_{\text{C}_6\text{H}_6}$ values for the electron in 2-propanol vs. corresponding results of Anbar and Hart⁵ for the hydrated electron.

In a plot of $\log k_{\text{C}_6\text{H}_6}$ values for the monosubstituted benzenes against mean Hammett σ_{para} values (Figure 3), there is considerable scatter about a best straight line. This scatter may also be noted in the study of the hydrated electron.⁵ However, if the spread of all calculated σ values⁶ is taken into account, the $\log k_{\text{C}_6\text{H}_6}$ values, with the exception of chloro-, bromo- and iodobenzene, conform to a straight-line plot. The ρ value is 3.1 and may be compared with $\rho = 4.8$ obtained by Anbar and Hart for the reactions of the hydrated electron.⁵ The relatively large deviation of bromobenzene and iodobenzene from the best straight line was also noted in the study of the hydrated electron. An explanation put forward in this case was that there may be a direct interaction between the hydrated electron and the substituent which would contribute toward an increased reaction rate. Another rationalization may be suggested. The gas phase electron affinity of the chlorine, bromine, and iodine atoms⁷ exceeds the dissociation energy of the corresponding carbon-halide bond.⁸ If (1) is in fact an equilibrium,

(5) M. Anbar and E. J. Hart, *J. Am. Chem. Soc.*, **86**, 5633 (1964).

(6) σ_{para} values are taken from the review of H. Van Bekkum, P. E. Verkade, and B. M. Wepster, *Rec. Trav. Chim.*, **78**, 815 (1959).

(7) F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press Inc., New York, N. Y., 1957, p 149.

(8) T. L. Cottrell, "The Strengths of Chemical Bonds," Butterworth and Co. Ltd., London, 1954, pp 211, 213, 277.

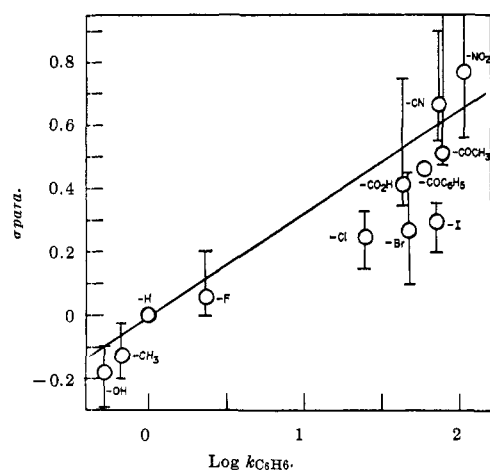


Figure 3. Plot of Hammett σ_{para} functions vs. $\log k_{C_6H_6}$ values for the electron in 2-propanol. The mean values for the σ_{para} functions are taken from the review of Van Bekkum, *et al.*;⁶ The vertical lines encompass the spread of values for these functions.

then dissociation of the carbon-halide bond may occur before the back reaction and enhance the observed rate of the electron-capture process.

A similarly satisfactory correlation between reactivity and σ values may be observed in the case of the disubstituted benzenes. The ρ values for the chlorobenzene and phenol series are 0.86 and 3.6, respectively (see Figure 4). However, as was the case in the monosubstituted benzene series, the chloro and bromo derivatives are somewhat anomalous and show a reactivity which is greater than would be expected of aromatic compounds containing substituents with these σ values. In the application of the Hammett equation to aromatic substitution, the effect of a second substituent is generally additive as long as there is no additional resonance interaction between the second substituent and the reactive center.³ In the reactions of the solvated electron in 2-propanol, this additivity rule does not hold. It appears that a series containing

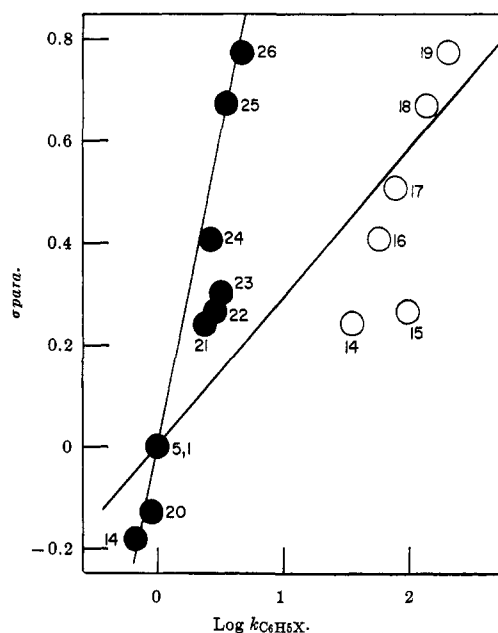


Figure 4. Plot of Hammett σ_{para} functions⁶ vs. $\log k_{C_6H_5X}$ values for monosubstituted chlorobenzenes (●) and phenols (○). $k_{C_6H_5X}$ is the reactivity relative to the parent chlorobenzene or phenol.

a substituent which activates the ring toward the solvated electron (*e.g.*, the chlorobenzenes) has a lower ρ value than the monosubstituted series. In the case of the nitrobenzenes, where the nitro group strongly activates the ring, the rate constant is almost insensitive to the second substituent. In a series where the substituent deactivates the ring, (*e.g.*, the phenols) the rate constant is more sensitive to the second substituent and an enhanced ρ is observed. These observations parallel those made by Anbar and Hart on the reactivity of the hydrated electron.⁵

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