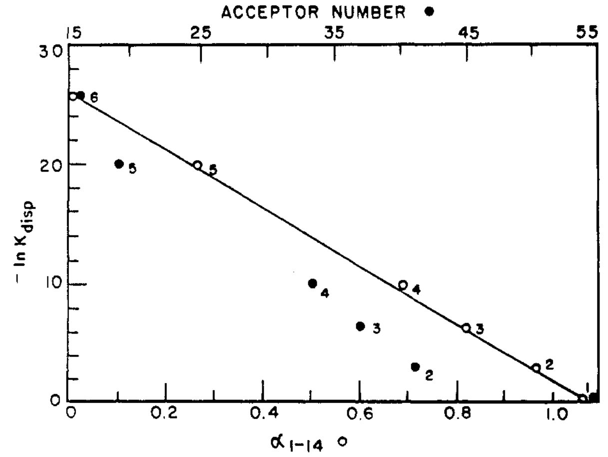


Figure 3. Plot of the negative logarithm of K_{disp} for the reduction of AQS in various solvents vs. the acceptor number (closed circles[34,35]) and α_{1-14} (open circles[32,33]) scales of solvent polarity. Numbers indicate the solvent: 1, water; 2, methanol; 3, ethanol; 4, 2-propanol; 5, acetonitrile; and 6, dimethylformamide.

nificance of this correlation is substantiated by reports from other laboratories. Hydrogen-bonded radical anions of anthraquinone with 2-propanol have been directly observed by electron spin resonance.[31] Furthermore, hydrogen-bonded intermediates have been implicated in kinetic studies of anthraquinone radical anion protonation.[34]

Two other solvent parameters have been correlated with the data in Table I. The Gutman acceptor number[35,36] is a measure of the Lewis acidity of the solvent, and so should reflect the ability to solvate anions. Linear regression of the data for AQS with this parameter gave a poorer correlation (r = 0.963) with the data point from aqueous solutions giving the largest deviation. Swain's A and B numbers,[37] which have been obtained by extensive correlation with many solvent processes, are associated with anion and cation solvating ability, respectively. The data in Table I were fit to Swain's numbers using nonlinear regression with the following expression:

$$\ln K_{disp} = aA + bB + c \qquad (4)$$

The ratio of b/a for the best fit was −0.29 with a correlation coefficient of 0.992. It is interesting to note that Swain finds that the α term of Taft is best expressed by a similar ratio, −0.36. This further suggests that hydrogen-bonding acidity is a major reason for the observed changes in disproportionation equilibria.

The high degree of correlation of the thermodynamic data with hydrogen-bonding donicity and the poor correlation of a solvent scale that relates to solvent polarity (i.e., the Gutman number) indicates that hydrogen bonding is the major factor in the observed changes in stability of the radical anion in protic solvents at very high values of pH. Solvents which form stronger hydrogen bonds facilitate disproportionation. The high sensitivity of the equilibrium constant to solvent effects in part reflects the greater stabilization of the dianion by hydrogen bonding. In addition, the radical anion is destabilized with respect to disproportionation by charge delocalization from hydrogen bonding. For benzoquinone it has been shown that the former is the greater effect.[24] The correlation for hydrogen bonding is sufficiently high that predictions of stability in other, untested solvents may be readily applicable. Thus, for the first time, it should be possible to extrapolate the large amount of electrochemical data obtained in aprotic solvents to aqueous solutions. Furthermore, hydrogen bonding may be important in the observed disproportionation of other radicals. For example, oxygen shows similar electrochemical behavior in basic, aqueous solution, and the superoxide anion can be stabilized by an organic layer at the electrode surface.[38]

Registry No. AQ, 84-65-1; AQS, 84-48-0; 2,6-AQS, 84-50-4.

---

[34] Wightman, R. M.; Cockrell, J. R.; Murray, R. W.; Burnett, J. N.; Jones, S. B. *J. Am. Chem. Soc.* **1976**, *98*, 2562.

[35] Mayer, U.; Gutmann, V.; Gerger, W. *Monatsh. Chem.* **1975**, *106*, 1235.

[36] Gutmann, V. *Coord. Chem. Rev.* **1976**, *18*, 225.

[37] Swain, C. G.; Swain, M. S.; Powell, A. L.; Alunni, S. *J. Am. Chem. Soc.* **1983**, *105*, 502.

[38] Chevalet, J.; Roulle, R.; Gierst, L.; Lambert, J. P. *J. Electroanal. Chem.* **1972**, *39*, 201.

Kinetics and Mechanism of the Oxidation of Substituted Benzaldehydes by *N*-Bromobenzamide

Kalyan K. Banerji

Department of Chemistry, University of Jodhpur, Jodhpur 342 001, India

Received March 11, 1986

The oxidation of eighteen meta- and para-substituted benzaldehydes by *N*-bromobenzamide (NBB), to the corresponding benzoic acid, is first order with respect to the aldehyde, NBB, and hydrogen ion. The oxidation of benzaldehyde exhibited a substantial primary kinetic isotope effect ($k_H/k_D = 5.3 \pm 0.1$). Addition of benzamide has no effect on the reaction rate. $(PhCONH_2Br)^+$ has been postulated as the reactive oxidizing species. The rates of the oxidation of meta- and para-substituted benzaldehydes were separately correlated in Taft's and Swain's dual substituent parameter equations. For para-substituted aldehydes, the best correlation was obtained with σ_I and $\sigma_R{}^+$ values, while meta-substituted compounds correlate with σ_I and $\sigma_R{}^0$ values. The reaction constants have negative values. A mechanism involving transfer of a hydride ion from the aldehyde to the oxidant, in the rate-determining step, has been proposed.

Kinetics of the oxidation of organic compounds by *N*-halogeno amides have received considerable attention recently.[1-8] Similarly the oxidations of aromatic aldehydes by transition-metal ions have been reported.[9] There seems to be no report about the kinetics and mechanism of the oxidation of aromatic aldehydes by an *N*-halogeno amide, though the reactions of *N*-bromosuccinimide (NBS) with aromatic aldehydes and their derivatives have been reported to be synthetically useful.[10] We have studied the oxidation of a series of eighteen meta- and para-substituted benzaldehydes by *N*-bromobenzamide (NBB) in aqueous acetic acid solution, in the presence of perchloric acid. Attempts have been made to study the correlation of structure and reactivity in this reaction.

Experimental Section

m-Acetamidobenzaldehyde was prepared[11] by the reduction of *m*-nitrobenzaldehyde with $SnCl_2$–HCl to give the aminobenzaldehyde, followed by the acetylation of the amine with acetic anhydride and phosphoric acid. The other aldehydes (Aldrich or Fluka) were purified by either recrystallization or distillation. NBB was prepared by a reported method.[12] [^{2}H]Benzaldehyde (PhCDO) was prepared[13] by the reduction of benzil by lithium aluminum deuteride (Fluka) to give the diol, followed by the oxidation of the diol by lead tetraacetate. Acetic acid was refluxed with potassium dichromate for 6 h and distilled before use.

Product Analysis. Freshly distilled benzaldehyde (3.15 g, 0.03 mol) and NBB (2.0 g, 0.01 mol) were made up to 100 mL in 1:4 (v/v) acetic acid–water, in the presence of 0.5 M perchloric acid. The reaction mixture was allowed to stand for ca. 10 h to ensure completion of the reaction. The reaction was extracted with ether (3 × 100 mL). The ether solution was extracted with a saturated solution of $NaHCO_3$. The $NaHCO_3$ extract was concentrated by evaporating the solvent at 80 °C. The concentrated solution was acidified with concentrated HCl and cooled in ice to furnish the crude acid (1.2 g, 88%), which was recrystallized from hot water to produce pure benzoic acid (0.95 g).

Stoichiometry. To determine the stoichiometry, benzaldehyde was treated with an excess of NBB. When the reaction was complete, unreacted NBB was determined iodometrically. Several determinations, using substituted benzaldehydes, indicated a 1:1 stoichiometry.

Kinetic Measurements. Pseudo-first-order conditions were maintained by keeping a large excess of the aldehyde over NBB. Mercury(II) acetate (0.00 M) was added to each reaction mixture to prevent liberation and further reactions of bromine.[1] Preliminary experiments showed that the rate of reaction is not sensitive to ionic strength (0.1–1.0 M), and hence no attempt was made to keep the ionic strength constant. The reactions were carried out in flasks blackened from the outside to prevent any photochemical reactions. The temperature was kept constant to ±0.1 K. The reactions were followed iodometrically for up to 70% of the reaction. The solvent was 1:1 (v/v) acetic acid–water. The pseudo-first-order rate constant, k_1, was determined from the linear plots of log [NBB] vs. time. The specific rate constant, k, was obtained from the relation $k = k_1/[\text{aldehyde}][H^+]$. Duplicate kinetic runs showed that the rates are reproducible to within ±4%. The average error limits in the values of ΔH^* and ΔS^* are ±3 kJ mol^{-1} and ±5 J mol^{-1} K^{-1}, respectively.

Multiple linear regressions were carried out with an Apple IIe microcomputer.

Table I. Rate Constants of the Oxidation of Benzaldehyde by NBB at 298 K

[PhCHO], M	10^3[NBB], M	[H$^+$], M	$10^5 k_1$, s^{-1}
0.10	5.0	0.5	1.05
0.20	5.0	0.5	2.06
0.30	5.0	0.5	3.00
0.50	5.0	0.5	5.25
0.75	5.0	0.5	7.80
1.00	5.0	0.5	11.2
0.50	2.0	0.5	5.42
0.50	3.5	0.5	5.25
0.50	7.5	0.5	5.00
0.50	10.0	0.5	5.32
0.50	15.0	0.5	5.17
0.50	5.0	0.1	1.07
0.50	5.0	0.2	2.00
0.50	5.0	0.3	3.07
0.50	5.0	0.7	6.93
0.50	5.0	0.9	9.42
0.50	5.0	1.0	10.8

Table II. Kinetic Isotope Effect in the Oxidation of Benzaldehyde by NBB[a]

[aldehyde], M	type	$10^6 k_1$, s^{-1}	
0.1	^{1}H	10.5	
0.2	^{1}H	20.6	$10^5 k_H = 21.1 \pm 0.4$ M^{-2} s^{-1}
0.4	^{1}H	43.1	
0.1	^{2}H	2.00	
0.2	^{2}H	3.95	$10^5 k_D = 3.98 \pm 0.02$ M^{-2} s^{-1}
0.3	^{2}H	5.97	

$k_H/k_D = 5.30 \pm 0.10$

[a] [NBB] = 0.005 M, [H$^+$] = 0.5 M; temperature, 298 K; k_H and $k_D = k_1/[\text{aldehyde}]\,[H^+]$.

Table III. Effect of Benzamide on the Oxidation of Benzaldehyde by NBB[a]

10^2[benzamide], M	0	2	3	4	5
$10^5 k_1$, s^{-1}	5.25	5.30	5.13	5.40	5.40

[a] [NBB] = 0.005 M, [PhCHO] = 0.5 M; [H$^+$] = 0.5 M; temperature, 298 K.

Results

The rate laws and other data were obtained for all the compounds investigated. Since results are similar only representative data are reproduced here.

The oxidation of aromatic aldehydes by NBB results in the formation of corresponding benzoic acid (1).

$$ArCHO + PhCONHBr + H_2O \rightarrow ArCOOH + PhCONH_2 + HBr \quad (1)$$

Rate Laws. The oxidation of the aromatic aldehydes by NBB is first order with respect to NBB. Further, the pseudo-first-order rate constant is independent of initial concentration of NBB. The variation in the concentration of the aldehyde and hydrogen ion shows that the reaction is first order with respect to the aldehyde and hydrogen ion also (Table I).

Kinetic Isotope Effect. To ascertain the importance of the cleavage of the aldehydic C–H bond in the rate-determining step, the oxidation of [^{2}H]benzaldehyde was studied. The results show the presence of a substantial primary kinetic isotope effect (Table II).

Effect of Benzamide. Addition of benzamide does not affect the rate of reaction (Table III).

Effect of Substituents. The rates of oxidation of benzaldehyde, nine para-substituted and eight meta-monosubstituted benzaldehydes were determined at different

---

(1) Mukherjee, J.; Banerji, K. K. *J. Org. Chem.* **1981**, *46*, 2323.

(2) Bhatia, I.; Negi, S. C.; Banerji, K. K. *J. Chem. Res. Symp.* **1981**, 360; *J. Chem. Res. Miniprint* **1981**, 3966.

(3) Sharma, V.; Banerji, K. K. *J. Chem. Res. Symp.* **1985**, 340; *J. Chem. Res. Miniprint* **1985**, 3551.

(4) Negi, S. C.; Banerji, K. K. *J. Org. Chem.* **1983**, *48*, 3329.

(5) Venkatasubramanian, N.; Thiagarajan, V. *Tetrahedron Lett.* **1967**, 3349.

(6) Thiagarajan, V.; Venkatasubramanian, N. *Can. J. Chem.* **1969**, *47*, 694.

(7) Gopalakrishnan, G.; Pai, B. R.; Venkatasubramanian, N. *Indian J. Chem., Sect. B* **1980**, *19*, 293.

(8) Srinivasan, N. S.; Venkatasubramanian, N. *Tetrahedron* **1974**, *30*, 419.

(9) Sen Gupta, K. K.; Dey, S.; Sen Gupta, S.; Banerji, A. *J. Chem. Soc., Perkin Trans. 2* **1985**, 1503 and references cited therein.

(10) Grundmann, C.; Richter, R. *J. Org. Chem.* **1968**, *33*, 476.

(11) Davey, W.; Gwilt, J. R. *J. Chem. Soc.* **1957**, 1008.

(12) Hauser, C. R.; Renfrow, W. B., Jr. *J. Am. Chem. Soc.* **1923**, *59*, 121.

(13) Wiberg, K. B. *J. Am. Chem. Soc.* **1954**, *76*, 5371.

Table IV. Rate Constants and the Activation Parameters of the Oxidation of Substituted Benzaldehydes by NBB[a]

subst	10^6k, M^{-2} s^{-1}					ΔH^*,[b] kJ mol^{-1}	ΔS^*,[b] J mol^{-1} K^{-1}
	293 K	298 K	303 K	308 K	313 K		
H	140	206	303	440	615	56.0	−140
p-Me	1070	1450	2020	2650	3450	47.7	−142
p-NHCOMe	14300	18600	25000	34100	50000	40.7	−144
p-OMe	40500	52500	71000	91600	116000	40.6	−136
p-F	430	682	865	1710	2600	52.8	−131
p-Cl	120	200	325	530	835	74.2	−69
p-Br	87.8	144	238	390	638	74.4	−71
p-NO_2	1.03	2.06	4.05	8.04	15.3	101	−15
p-CN	2.00	3.83	7.45	13.5	25.3	96.3	−27
p-COOMe	8.70	15.0	26.0	44.0	72.0	79.6	−73
m-Me	265	340	480	633	848	46.4	−158
m-OMe	94.0	161	272	371	573	66.5	−97
m-F	18.1	28.0	44.8	66.2	91.0	61.0	−130
m-Cl	14.8	25.4	39.5	58.9	91.0	66.4	−113
m-Br	15.5	26.2	40.0	62.9	88.9	64.7	−118
m-NO_2	1.49	3.00	5.64	10.7	18.0	92.2	−44
m-CN	3.00	5.52	10.3	14.9	26.5	79.4	−81
m-NHCOMe	56.4	90.0	134	197	285	62.6	−115

[a] $k = k_1/[\text{aldehyde}]\,[H^+]$. [b] At 298 K.

Table V. Correlation of the Rates of Oxidation of Substituted Benzaldehyde by NBB with Dual Substituent Parameters[a]

subst constants	para-substituted				meta-substituted			
	ρ_I	ρ_R	SD	*f*	ρ_I	ρ_R	SD	*f*
σ_I, $\sigma_R{}^0$	−2.56	−5.52	0.48	0.3	−2.53	−1.23	0.02	0.02
σ_I, $\sigma_R{}^{BA}$	−2.66	−4.56	0.36	0.25	−2.57	−0.98	0.04	0.04
σ_I, $\sigma_R{}^{-}$[b]	−1.86	−3.32	0.54	0.37	−2.39	−0.80	0.08	0.08
σ_I, $\sigma_R{}^+$	−2.38	−3.00	0.02	0.014	−2.54	−0.66	0.10	0.11
Swain et al.[c]	−0.7	−1.63	0.31	0.21	−1.49	−0.38	0.08	0.10

[a] Temperature 298 K, SD = root mean square of the standard deviation, f = SD/root mean square of log k/k_0, σ_I and σ_R values are from ref 18. [b] Data for NHCOMe not considered, no $\sigma_R{}^-$ value is available. [c] Field and resonance substituent constants are from ref 19.

temperatures and the activation parameters were evaluated (Table IV).

Discussion

The linear correlation between log k at 293 K and 313 K (r = 0.9946, slope = 0.8859) for the oxidation of 18 aldehydes shows that all the compounds are oxidized by the same mechanism.[14] The value of isokinetic temperature is 527 K.

In acidified aqueous acetic acid solution of NBB, possible oxidizing species are NBB itself, HOBr, $PhCONBr_2$, Br_2, AcOBr, and their protonated forms. The absence of any effect of the parent amide on the reaction rate precludes a hydrolysis of NBB in the preequilibrium and rules out HOBr, $PhCONBr_2$, Br_2, and AcOBr as the reactive oxidizing species. This also rules out the initial formation of a hypobromite ester by nucleophilic attack on the carbonyl group. The strict first-order dependence of the reaction rate on NBB also rules out $PhCONBr_2$ and molecular bromine as the reactive oxidizing species. Thus the reactive species in this reaction appears to be the *N*-bromo amide itself or its protonated form. This is in contrast to the observation in the oxidations by NBS and *N*-bromoacetamide[1-7] where a retardation of rate on the addition of the parent amide was observed and the reactive species was postulated to be HOBr.

The linear increase in the reaction rate with an increase in the concentration of hydrogen ion suggests a protonation of NBB to give a stronger oxidant and electrophile (2).

$$PhCONHBr + H_3O^+ \rightleftarrows (PhCONH_2B)^+ + H_2O \quad (2)$$

Recently Sen Gupta et al.[9] suggested that in the oxidation by vanadium(V), the hydrated form of benzaldehyde participates in the reaction. However, in aqueous solutions the aromatic aldehydes are not hydrated to any appreciable extent,[15,16] and it is unlikely that the hydrate form of the aromatic aldehyde is involved in the oxidation process.

The value of primary kinetic isotope effect (k_H/k_D = 5.3) compares favorably with the values of 4.8 and 4.3 obtained in the oxidations by vanadium(V)[9] and chromic acid,[17] respectively. This result confirms that the aldehydic C–H bond is cleaved in the rate-determining step.

Correlation Analysis of Reactivity. Since the rates of oxidation of the monosubstituted benzaldehydes failed to show satisfactory correlation with any single substituent parameter, the rates were subjected to analysis by Taft's[18] and Swain's[19] dual substituent parameter (DSP) equations. The rates of oxidation of the meta- and para-substituted benzaldehydes were separately correlated with σ_I and the four different σ_R substituent constants in Taft's equation[18] and with the field and resonance substituent constants of Swain et al.[19] The analyses were carried out by a multiple linear least-squares regression method. The results are summarized in Table V. Both the meta and para series of substituted benzaldehydes meet the minimal basic requirements of substituents for the analysis by DSP equations.[20] We did not use amino and dimethylamino substituents as these groups are liable to be protonated in acid solution and are not likely to behave as electron-

---

(14) Exner, O. *Prog. Phys. Org. Chem.* **1973**, *10*, 411.

(15) Greenzaid, P. *J. Org. Chem.* **1973**, *38*, 3164.

(16) Bover, W. J.; Aumen, P. *J. Chem. Soc., Perkin Trans. 2* **1973**, 786.

(17) Wiberg, K. B.; Mill, T. *J. Am. Chem. Soc.* **1958**, *80*, 3022.

(18) Dayal, S. K.; Ehrenson, S.; Taft, R. W. *J. Am. Chem. Soc.* **1972**, *94*, 9113.

(19) Swain, C. G.; Unger, S. H.; Rosenquist, N. R.; Swain, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 492.

(20) Shorter, J. *Correlation Analysis of Organic Reactivity*; Research Studies: Chichester, 1982; p 50.

Table VI. Temperature Dependence of the Reaction Constants[a]

temp, K	ρ_I	ρ_R[b]	λ	R	SD	f
		Para-Substituted				
293	−2.58	−3.10	1.20	0.9999	0.01	0.007
298	−2.38	−3.00	1.26	0.9997	0.02	0.02
303	−2.23	−2.89	1.30	0.9995	0.05	0.04
308	−2.01	−2.81	1.40	0.9997	0.02	0.01
313	−1.85	−2.74	1.48	0.9995	0.04	0.03
		Meta-Substituted				
293	−2.74	−1.27	0.46	0.9994	0.02	0.02
298	−2.53	−1.23	0.49	0.9998	0.02	0.02
303	−2.40	−1.07	0.45	0.9997	0.02	0.02
308	−2.28	−1.02	0.45	0.9989	0.03	0.04
313	−2.18	−1.02	0.47	0.9952	0.07	0.08

[a] R = coefficient of multiple correlation, SD = root mean square of standard deviation, $\lambda = \rho_R/\rho_I$, f = SD/root mean square of log k/k_0. [b] ρ_R is ρ_R^+ and ρ_R^0 for the para- and meta-substituted compounds, respectively.

donor groups by resonance. Instead we used the acetylamido (NHCOMe) group.

The results show that the rates of para-substituted aldehydes show excellent correlation with σ_I and σ_R^+ values. The correlations with the other three σ_R values and in Swain's equation are relatively poor. We have used the standard deviation (SD) and f as the measures of goodness of fit. f has been defined by Dayal, Ehrenson, and Taft[18] as f = SD/RMS, where RMS is the root mean square of the data points (here log k/k_0). The coefficient of multiple linear regression (R) was also determined. The comparison of f values shows that f is smaller for σ_R^+ scale than those for other scales by factors of ~20 to ~40. Therefore it is apparent that the rates of the oxidation of para-substituted benzaldehydes by NBB correlate best with σ_I and σ_R^+.

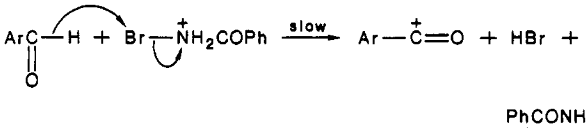
The rates of meta-substituted benzaldehydes show excellent correlation with σ_I and σ_R^0, though the discriminating factor for the precision of fit with the other σ_R scales or with Swain's equation is not as sharp as in the case of para-substituted compounds. In fact, the correlations with σ_R^{BA} and σ_R^- meet the requirement[21] for a satisfactory fit ($f < 0.1$). Even the correlation with the σ_R^+ scale and in Swain's equation are not very poor. This agrees with the observation of Ehrenson, Brownlee, and Taft[21] that the correlation of meta-substituted compounds is generally best with σ_R^0 and meta-substituted compounds are less discriminating. It has been observed in many reactions that the meta- and para-substituted compounds correlate with different σ_R scales.[21]

The reaction constants and statistical data at different temperatures are given in Table VI. The relatively large values of λ^p (1.20–1.48) show that in the oxidation of para-substituted benzaldehydes the resonance effect is predominating. The selectivity of the reaction is decreased at higher temperatures, but this decrease is more pronounced for the inductive effect as compared to the resonance effect. This is reflected in the gradual increase in the value of λ^p with temperature.

In the oxidation of the meta-substituted compounds, the value of λ^m is ca. 0.46 and shows the relatively greater importance of the inductive effect. This is on the expected lines. In this case, the decrease in the reaction constants is of similar order, resulting in almost same value of λ^m at different temperatures. The ratio of λ^m/λ^p is ca. 0.35.

The plots between the observed and calculated values of log k/k_0 for the para- and meta-substituted compounds are linear (r = 0.9976 and 0.9984, respectively).

Mechanism. The large negative reaction constants, correlation of the rates of the oxidation of the para-substituted compounds with σ_R^+ values and a substantial deuterium isotope effect suggest a considerable carbocation character in the transition state. The observed value of the primary kinetic isotope effect is rather large for the nonlinear transition state implied in the ester mechanism. The above results, thus, suggest the transfer of a hydride ion, in the rate-determining step, from the aromatic aldehyde to the protonated NBB (3).



(3)

$$\mathrm{Ar{-}\overset{+}{C}{=}O + H_2O \xrightarrow{fast} ArCOOH + H^+} \quad (4)$$

The above mechanism is supported by the observed negative entropy of activation also.

Acknowledgment. The financial support to this study by the University Grants Commission, India, is gratefully acknowledged. Thanks are due to Prof. J. Shorter, University of Hull, U.K., and Dr. R. P. Tripathi of USIC, Jodhpur for the help in writing the program for multiple linear regression.

Registry No. NBB, 19964-97-7; PhCHO, 100-52-7; Me-*p*-C_6H_4CHO, 104-87-0; MeCONH-*p*-C_6H_4CHO, 122-85-0; MeO-*p*-C_6H_4CHO, 123-11-5; F-*p*-C_6H_4CHO, 459-57-4; Cl-*p*-C_6H_4CHO, 104-88-1; Br-*p*-C_6H_4CHO, 1122-91-4; O_2N-*p*-C_6H_4CHO, 555-16-8; NC-*p*-C_6H_4CHO, 105-07-7; MeOCO-*p*-C_6H_4CHO, 1571-08-0; Me-*m*-C_6H_4CHO, 620-23-5; MeO-*m*-C_6H_4CHO, 591-31-1; F-*m*-C_6H_4CHO, 456-48-4; Cl-*m*-C_6H_4CHO, 587-04-2; Br-*m*-C_6H_4CHO, 3132-99-8; O_2N-*m*-C_6H_4CHO, 99-61-6; NC-*m*-C_6H_4CHO, 24964-64-5; MeCONH-*m*-C_6H_4CHO, 59755-25-8; D_2, 7782-39-0.

---

(21) Ehrenson, S.; Brownlee, R. T. C.; Taft, R. W. *Prog. Phys. Org. Chem.* 1973, *10*, 1.