The erythro sulfide benzoate resisted oxidation to the sulfone. The sulfide–alcohol **3** could be oxidized with **15** at 65° to yield *erythro*-**9**, mp 129.5–131.0°.

Anal. Calcd for $C_{20}H_{18}O_3S$: C, 70.88; H, 5.36. Found: C, 70.93; H, 5.34.

In a crossover run, the anion of **13** was prepared as before (22 mmol). To this material benzaldehyde was added until no color remained. To this mixture, *p*-chlorobenzaldehyde (2.0 g) was added and the mixture was stirred for 3 hr. Chromatography on Florisil gave **16**, **1** (0.4 g), and several fractions of mixed **8′** and **13**. With pure benzene as eluent, **8′**, 0.15 g, mp 151–152° was isolated, which was identical with authentic material prepared separately.

Procedure for the Pyrolyses.—Equal quantities (*ca.* 0.050 g) of two of the four sulfoxides, **4–7**, were dissolved in *ca.* 1 ml of DMSO in an nmr tube and placed in an oil bath at 119 ± 3° A trace of pyridine was added to absorb any acid formed. The nmr tube was withdrawn at invervals and the diminishment of the characteristic nmr signals[6] of **4–7** was followed by nmr integration (the average of 3–5 traces in each of eight points was taken). As **4–7** diminished, the spectrum of deoxybenzoin appeared, identical with that of authentic material.

Registry No.—**2** benzoate, 32120-62-0; **3**, 10277-57-3; **3** benzoate, 32120-64-2; **4**, 28455-74-5; **4′**, 32120-77-7; **5**, 28455-94-9; **6**, 28455-75-6; **6** benzoate, 32120-68-6; **7**, 32120-69-7; **7** benzoate, 32120-70-0; **7′**, 28455-78-9; **8**, 28520-74-3; **8** benzoate, 32120-73-3; **8′**, 32120-74-4; **9**, 28520-75-4; **16**, 32120-75-5; **17**, 32120-76-6.

Substituent Effects on the Half-Wave Potentials of Chalcones in Dimethylformamide

MARY L. ASH,[1] FRANK L. O'BRIEN, AND DAVID W. BOYKIN, JR.*[2]

Department of Chemistry, Georgia State University, Atlanta, Georgia 30303

Received March 12, 1971

The reduction half-wave potentials of two series of substituted *trans*-chalcones (I) have been determined in dimethylformamide. One series contains substituents in ring A, included in this series are five ortho-substituted compounds, and the other contains substituents in ring B. The first polarographic reduction wave was studied and it was shown to be a one-electron, diffusion-controlled process. Polarographic data and preliminary cyclic voltametric data indicate that the electrochemical reduction involves rapid chemical reaction of the one-electron transfer product. A very good linear free-energy relationship for substituents in ring A, excluding the ortho substituents, was obtained between $E_{1/2}$ and σ ($r = 0.997$). The linear free-energy relationship for substituents in ring B obtained between $E_{1/2}$ and σ was virtually as good ($r = 0.985$). The $E_{1/2}$ values for the ortho substituents in ring A were positively displaced by about 35 mV from their para isomers. The ortho isomers show a good linear relationship when $E_{1/2}$ is plotted against σ_p ($r = 0.982$). The $E_{1/2}$ data were also treated with the Swain–Lupton expression and generally poorer correlations were obtained with it than those obtained with the Hammett expression. Comparisons of these linear free-energy relationships with others previously reported for the chalcone system are made.

A number of linear free-energy relationships have been established for several α,β-unsaturated ketone systems,[3] including the chalcones. The effect of substituents on ultraviolet spectra,[4] basicities,[5] carbonyl stretching frequencies of chalcones,[6] and dipole moments[7] of chalcone types have been reported. The results of a wide variety of investigations on the effect of substituents on the polarographic half-wave potentials for the reduction of carbonyl compounds have been reported for numerous systems.[8a] Furthermore, there are many examples of correlation of their half-wave potentials with Hammett substituent constants.[8a] For example, good correlations of reduction half-wave potentials with Hammett σ constants were observed for acetophenones[9] and benzophenones.[10]

The effect of substituents on the reduction half-wave potentials of chalcones and chalcone analogs in aqueous media has been reported.[11] The electrochemical reduction mechanism of chalcone in aqueous alcohol mixtures has been studied extensively and is well summarized in a recent publication.[12] The reduction process involves several chemical reactions, is dependent upon hydrogen ion activity, and is further complicated by the formation of organomercury compounds. Electrochemical studies in nonaqueous solvents on chalcone also have been reported;[13] however, a systematic study of substituent effects in a nonaqueous medium has not been carried out. In acetonitrile and in dimethylformamide, chalcone is reduced to a carbanion radical which undergoes rapid polymerization.[13] No evidence is reported for the other reactions which were observed in aqueous solvents. The absence of the more complicated chemical reactions in nonaqueous media should lead to more reliable relationships between half-wave potentials and structure. The elucidation of the structure–reactivity–potential relationship of this relatively simple α,β-unsaturated ketone system will enhance the understanding of the reduction of this system and provide a model for other similar but more complex systems, some

---

[1] This work represents a partial fulfillment of the requirements for the B.S. degree with honor by M. L. A.

[2] Author to whom inquiries should be addressed.

[3] (a) J. R. Dimmock, P. L. Carter, and P. D. Ralph, *J. Chem. Soc. B*, 698 (1968); (b) S. Toma and A. Perjessy, *Chem. Zvesti*, **23**, 343 (1969); (c) R. W. Woodard and D. W. Boykin, Jr., *Chem. Commun.*, 628 (1970).

[4] (a) W. B. Black and R. E. Lutz, *J. Amer. Chem. Soc.*, **77**, 5134 (1955); (b) H. H. Szmant and A. J. Basso, *ibid.*, **74**, 4397 (1952).

[5] D. S. Noyce and M. J. Jorgenson, *ibid.*, **84**, 4312 (1962).

[6] (a) A. Perjessy, *Chem. Zvesti*, **23**, 905 (1969); (b) N. L. Silver and D. W. Boykin, Jr., *J. Org. Chem.*, **35**, 759 (1970).

[7] S. V. Tsukerman, V. P. Izvekov, and V. F. Lavrushin, *Zh. Fiz. Khim.*, **42**, 2159 (1968).

[8] P. Zuman, "Substituent Effects in Organic Polarography," Plenum Press, New York, N. Y., 1967: (a) Chapter 3; (b) p 74; (c) p 40; (d) p 75 ff.

[9] D. M. Coulson, W. R. Crowell, and S. K. Tendrick, *J. Amer. Chem. Soc.*, **79**, 1354 (1957).

[10] N. Fuson, M. L. Josien, and E. M. Shelton, *ibid.*, **76**, 2526 (1954).

[11] (a) V. F. Lavrushin, V. D. Bezuglyi, and G. G. Belous, *Zh. Obshch. Khim.*, **33**, 1711 (1963); (b) V. D. Bezuglyi, V. F. Lavrushin, and G. G. Belous, *ibid.*, **35**, 606 (1965); (c) S. Stankoviansky, A. Beno, S. Toma, and E. Gono, *Chem. Zvesti*, **24**, 19 (1970).

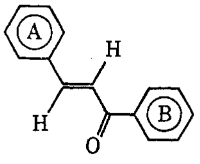
[12] A. R. Kyharova and P. Zuman, *J. Electroanal. Chem.*, **21**, 197 (1969).

[13] (a) S. Wawzonek and Z. Gunderson, *J. Electrochem. Soc.*, **111**, 324 (1964); (b) J. P. Zimmer, J. A. Richards, J. C. Turner, and D. Evans, *Anal. Chem.*, **43**, 1000 (1971).

of which may be related to those involved in biological processes.[14]

An interesting pattern of behavior is beginning to appear for the effects of substituents in both ring A and ring B of substituted *trans*-chalcones (I) and of other chalcone types. For example, p*K* data[5] and half-wave potential data[11] in aqueous media give about equally good correlations with substituents in both ring A and ring B; however, infrared data[6] and dipole moment data[7] for chalcones show a better correlation for substituents in ring A than in ring B. An ortho effect was observed on the p*K* for chalcones substituted in ring A; however, in contradistinction no such effect was detected on the carbonyl stretching frequency in the same series.

In order to further assess the relative effect of substituents in ring A and ring B on the properties of the *trans*-chalcone system, we have determined the polarographic half-wave potentials in dimethylformamide of two series of *trans*-chacones (I) one with substituents in ring A and the other with substituents in ring B. In addition, several chalcones with substituents in the ortho positions of ring A have been studied.



I

Polarography.—The reduction of all the chalcones in DMF at the dropping mercury electrode exhibited two well-defined waves. Since the first wave is of interest in this study, the following discussion will pertain only to it. The polarograms recorded for all compounds reported herein were similar except as noted.

The current varies linearly with the square root of mercury height on the limiting plateau, indicating that the process is diffusion controlled. The limiting current divided by concentration is constant over a concentration range of from 1.3×10^{-4} to 1.0×10^{-3} *M*. The diffusion current constant ($i_d/m^{2/3}t^{1/6}C$) for a representative compound, **17**, is 2.92. This is similar to a literature value for a confirmed one-electron process in the same solvent.[15] These observations indicate that the reduction is a one-electron diffusion controlled process uncomplicated by chemical reactions antecedent to the potential determining step.

Additional information on the overall mechanism was obtained from the preliminary cyclic voltammetric investigation of the parent chalcone **8**. At slow scan rates, 0.04 V/sec, a reduction wave is observed (Figure 1A). When the direction of scan is reversed, no corresponding oxidation process is observed but an oxidation wave is seen at a more positive potential (−0.2 V). At a scan rate of 4.0 V/sec, an oxidation wave attributable to the oxidation of the radical is observed (Figure 1B). As the scan rate is increased, the height of this wave increases with concomitant decrease in the height of the oxidation wave at −0.2 V. At 40.0 V/sec (Figure 1C), only the one oxidation wave is present. The various parameters of this wave meet the diagnostic criteria of Nicholson and Shain for a reversible one-electron wave with no chemical or adsorption complications.[16] If the reduction of the substituted chalcones proceed by the same general mechanism, the only direct effect of the chemical kinetics on the linear free energy studies will be a shift in the polarographic $E_{1/2}$ from the reversible value.

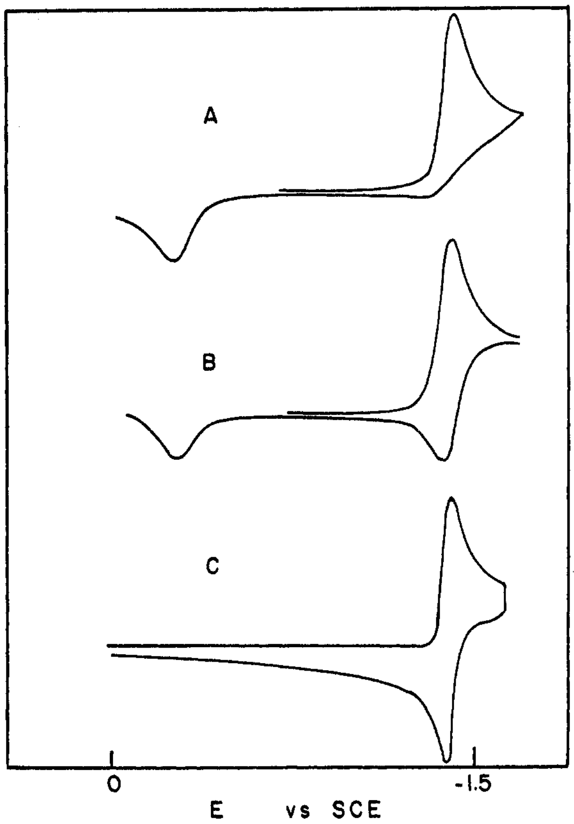


Figure 1.—Cyclic voltammograms of chalcone in DMF.

These combined results indicate that the electrochemical reduction of chalcone in DMF is to the anion radical which undergoes chemical reaction, one product of which is a more easily oxidizable species. Recently reported coulometric studies indicate that the final products of reduction of chalcone and other analogous α,β-unsaturated ketones are polymers consisting of from two to possibly four monomer units.[13b]

Preliminary chronoamperometric studies indicate that the overall follow-up chemical reaction is relatively fast and that it is at least second order with respect to chalcone. Complete results of these investigations will appear at a later date.

The Effect of Meta and Para Substituents in Ring A.—The $E_{1/2}$ data for compounds substituted in the meta and para positions of ring A (3- and 4-substituted chalcones) are shown in Table I. The influence of substituents on the reduction half-wave potential is that expected; the *p*-dimethylamino substituted chalcone (**1**) exhibits the most positive value whereas the 3,4-dichloro substituted compound exhibits the most negative one. The difference in $E_{1/2}$'s from the dimethylamino substituted compound to the 3,4-dichloro one is about 300 mV. The values of $E_{1/2}$ are correlated well with Hammett σ constants which were taken from

---

[14] *Cf.* (a) F. L. O'Brien and J. W. Olver, *Anal. Chem.*, **41**, 1810 (1969); (b) W. B. Geiger and J. E. Conn, *J. Amer. Chem. Soc.*, **67**, 112 (1945); (c) F. M. Menger and J. H. Smith, *ibid.*, **91**, 4211 (1969).

[15] J. L. Sadler and A. J. Bard, *J. Electrochem. Soc.*, **115**, 343 (1968).

[16] R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964).

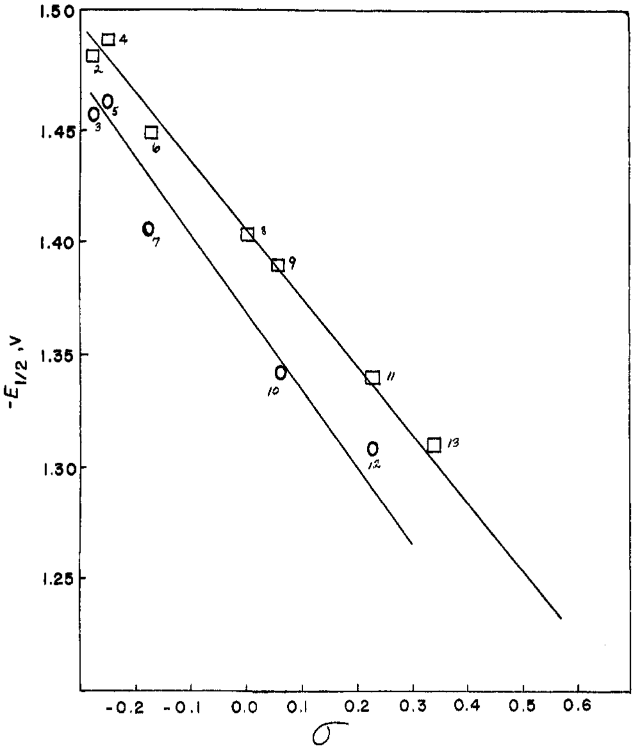


Figure 2.—Plots of $-E_{1/2}$ (V) *vs.* σ for ring A substituent: □, meta- and para-substituted compounds; ○, ortho-substituted compound.

TABLE I

HALF-WAVE POTENTIALS OF CHALCONES SUBSTITUTED IN RING A

Compd	Substituent	$-E_{1/2}$, V	Slope[a]
1	4-$(CH_3)_2N$	1.569	0.062
2	4-CH_3O	1.482	0.060
3	2-CH_3O	1.456	0.070
4	4-C_2H_5O	1.488	0.059
5	2-C_2H_5O	1.462	0.072
6	4-CH_3	1.450	0.062
7	2-CH_3	1.408	0.071
8	4-H	1.404	0.060
9	4-F	1.389	0.055
10	2-F	1.342	0.061
11	4-Cl	1.340	0.065
12	2-Cl	1.311	0.070
13	3-F	1.313	0.056
14	3,4-DiCl	1.268	0.075

[a] The slope of the plot of $-E$ (V) *vs.* log $[i/(i_d - i)]$.

the tabulation by Ritchie and Sager.[17] Least-squares and statistical treatment of the data were carried out as previously described and are given in Table II.[6b,18] The pertinent data are presented in graphical form in Figure 2.

The two points which correspond to compounds **1** and **14** deviate markedly from the least-squares line. The deviation of the amino group and its derivatives from electrochemical linear-free energy relationships is now well documented, although not well understood.[8b,19] The deviation in the system reported here is in the same direction as previously observed in other systems.[19] As has been pointed out, this deviation indicates a diminution of the mesomeric electron donor function of the group for the electrode reaction in comparison to homogeneous reactions. Speculations about the origin of the deviation have been presented by others and will not be repeated here.[8b,19]

TABLE II

RESULTS OF STATISTICAL TREATMENT USING σ CONSTANTS[a]

Series	*n*	*r*	*s*	*ρ*	*i*
Meta and para substituents in ring A	7[b]	0.997	0.0054	0.286	−1.407
Ortho substituents in ring A (σ_o*)	5	0.974	0.0176	0.220	−1.380
Ortho substituents in ring A (σ_p)	5	0.982	0.0148	0.305	−1.371
Ortho, meta, and para substituents in ring A	12[b]	0.953	0.0206	0.279	−1.393
Meta and para substituents in ring B	9	0.985	0.0138	0.289	−1.408

[a] *n* = number of points; *r* = correlation coefficient; *s* = standard deviation; *ρ* = slope of line; *i* = intercept. Unless otherwise noted Hammett σ constants were used in the calculations. [b] Compounds **1** and **14** were excluded in this calculation.

Zuman[8c] suggests that, when the errors of measurement of $E_{1/2}$'s have a range of ±5 mV, as is the case here, only deviations of greater than 20 mV should be considered significant. The deviation of the dimethylamino compound **1** from the least-squares line is about 35 mV; for this reason and because of the documented atypical electrochemical behavior of amino functions the value for it has been excluded from the statistical treatments. Although the deviation of the 3,4-dichloro compound **14** is only 18 mV, it has been excluded from the statistical treatments because the value of its current–potential slope (see Table I) suggests that its reduction mechanism probably differs from the other members of the series.

The value obtained for ρ in this work is of similar magnitude to that obtained by polarography on other carbonyl systems, although the previous work cited[9-11] was carried out in aqueous media. Meaningful assessment of the carbon–carbon double bond as a transmitting link during the electrode reaction cannot be made at present because of the apparent absence of $E_{1/2}$ data in DMF on systems such as acetophenones and benzaldehydes.[6b]

The new linear free energy relationship proposed by Swain and Lupton[20] provides a method by which an estimate of the contribution of resonance and field effects to the correlation may be made. Table III contains the results of correlations of $E_{1/2}$ data with the Swain *F* and *R* constants. The correlation obtained with the two-parameter approach (r = 0.915) is significantly poorer than the one obtained with the Hammett expression (r = 0.997). Because the Swain–Lupton report does not include treatment of $E_{1/2}$ data with their expression, previously reported $E_{1/2}$ data for acetophenones[9] and benzophenones[10] are included in Table III for comparison. In the four cases treated here, the Swain–Lupton treatment does not success-

---

(17) C. D. Ritchie and W. F. Sager in "Progress in Physical Organic Chemistry," Vol. 2, Interscience, New York, N. Y., 1964.

(18) H. H. Jaffe, *Chem. Rev.*, **53**, 191 (1953).

(19) P. Zuman, O. Exner, R. F. Rekker, and W. Th. Nauta, *Collect. Czech. Chem. Commun.*, **33**, 3213 (1968).

(20) C. G. Swain and E. C. Lupton, Jr., *J. Amer. Chem. Soc.*, **90**, 4328 (1968).

TABLE III

RESULTS OF STATISTICAL TREATMENT USING F AND R CONSTANTS[a]

Series	n	f	r	i	E	c	$\%R$
Meta and para substituents in ring A	7[b]	0.201 ± 0.047	0.315 ± 0.086	−1.404	0.331	0.917	50 ± 9
Ortho, meta, and para substituents in ring A	12[b]	0.185 ± 0.029	0.307 ± 0.054	−1.390	0.278	0.921	50 ± 6
Ortho substituents in ring A	5	0.160 ± 0.027	0.337 ± 0.051	−1.360	0.165	0.985	56 ± 6
Meta and para substituents in ring B	9	0.170 ± 0.033	0.227 ± 0.050	−1.403	0.315	0.934	44 ± 7
Acetophenones	10[c]	0.140 ± 0.035	0.251 ± 0.055	−0.977	0.337	0.899	54 ± 8
Benzophenones	6[d]	0.167 ± 0.038	0.253 ± 0.084	−1.132	0.297	0.939	34 ± 9

[a] Swain–Lupton field and resonance parameters; see ref 20. [b] Compounds **1** and **14** were not used in this correlation. [c] The $E_{1/2}$ values were taken from ref 9. The substituents were 4-H, 3-CH_3, 4-CH_3, 4-OH, 3-CH_3O, 4-CH_3O, 3-Cl, 4-Cl, 3-Br, 4-Br. The results of the least-squares treatment with σ: $s = 0.0139$; $r = 0.981$; $i = -0.997$; $\rho = 0.252$; $n = 10$. [d] The $E_{1/2}$ values were taken from ref 10. The substituents were 4-CH_3O, 4-CH_3, 4-H, 4-Cl, 4-Br, 3-Br. The results of the least-squares treatment with σ: $s = 0.0169$; $r = 0.974$; $i = -1.128$; $\rho = 0.254$; $n = 6$. n = number of points, f = regression coefficient for field parameter; r = regression coefficient for resonance parameter; i = intercept; E = standard error of estimate; c = multiple correlation coefficient; $\%R$ = per cent resonance contribution. These were calculated as indicated in ref 20; ϕ and ψ were calculated internally based upon the number of points used in the correlation.

fully treat the data as well as the simple Hammett approach. A similar finding was noted for treatment of carbonyl stretching frequency data.[6b] The contribution to the correlation by resonance as estimated by the Swain–Lupton approach for the chalcone system is 47%. The values for $\%R$ for the acetophenone (54%) and benzophenone (34%) correlation are not distinctly different from chalcone, suggesting, as has been previously noted,[6b] that the double bond transmits resonance effects efficiently.

The Effect of Ortho Substituents in Ring A.—Polarographic ortho effects may be attributed to changes in stability of the highest occupied molecular orbital and/or the lowest unoccupied molecular orbital which accepts the electron(s). Such alterations have been attributed[8d] to direct polar and steric effects; others[21] attribute them to an increase in the inductive and polar contribution of the substituent concomitantly with a decrease in resonance interaction.

The application of the Taft two-parameter expression[22] to electrochemical ortho-effect studies to assess steric factors has been questioned.[8d] More recently, Charton[23a] has shown that $E_s°$ constants do not represent steric influences and essentially represent only electrical factors. Further, Charton observes that σ_o^* constants do not represent an intrinsic general ortho electrical effect[23b] and that generation of a single set of generally applicable ortho-substituent constants is unlikely.[23c] We have tested the data for the five ortho-substituted (2′-substituted) chalcones shown in Table I with the Taft expression and indeed no correlation is observed ($r = 0.672$). Treatment of the data with σ_o^* alone gives a good correlation ($r = 0.974$) and treatment of the same five points with σ_p gives a better correlation ($r = 0.982$).

It is interesting that the ρ value ($\rho_o = 0.305$) for treatment of the five ortho compounds using σ_p is essentially the same as the slope for the line arising from the five corresponding para compounds ($\rho_p = 0.292$). The two lines differ only in displacement on the $E_{1/2}$ axis. The similarity of the Hammett slopes implies that the ortho and para substituents exhibit essentially the same electrical response during the electrochemical process. The positive displacement of $E_{1/2}$ for the ortho substituent with respect to the para isomers can be interpreted in terms of increased energy of the ground state for the ortho isomers. The positive displacement could be attributed to a decrease in coplanarity of the styryl moiety which would allow the inductive effect of the substituted styryl groups to come into play and decrease electron density at the reaction site (raise the energy of the highest occupied molecular orbital) and thus result in easier reduction. Although the slopes of the Hammett plots for the ortho and para lines are the same, it is possible that the positive shift of the $E_{1/2}$ value for the ortho isomer may reflect a change in the electrochemical mechanism in view of the consistently (except for **10**) high values for the current function–potential slopes.

It is interesting to note that an ortho effect in the chalcone system has been noted previously on pK's;[5] however, no effect was observed on the carbonyl stretching frequencies.[6b] The two studies in which ortho effects were detected involve the effect of substituents in cases in which reactive intermediates are being generated, carbonium ions in one case and anion–radicals in the other. That the carbonyl stretching frequency study did not reveal a detectable ortho effect reflects the relative insensitivity of the stretching vibration to substituents which are well removed from the reaction site and demonstrates that ortho effects are more readily detected in α,β-unsaturated ketone systems when electronic demands are intensified by charged intermediates.

Effects of Meta and Para Substituents in Ring B.—The effects of substituents in ring B (3′ and 4′ substitution) on the reduction half-wave potentials of the compounds shown in Table II were studied. The $E_{1/2}$'s for these compounds are correlated well with Hammett σ constants ($r = 0.985$) (see Table III and Figure 3). This correlation is essentially as good as, although slightly poorer than, the one obtained for the values in ring A (0.997). A similar relationship of ring

---

(21) W. W. Hussey and A. J. Diefenderfer, *J. Amer. Chem. Soc.*, **89**, 5359 (1967).

(22) R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, p 565.

(23) (a) M. Charton, *J. Amer. Chem. Soc.*, **91**, 615 (1969); (b) *ibid.*, **91**, 624 (1969); (c) M. Charton and B. I. Charton, *J. Org. Chem.*, **36**, 260 (1971).

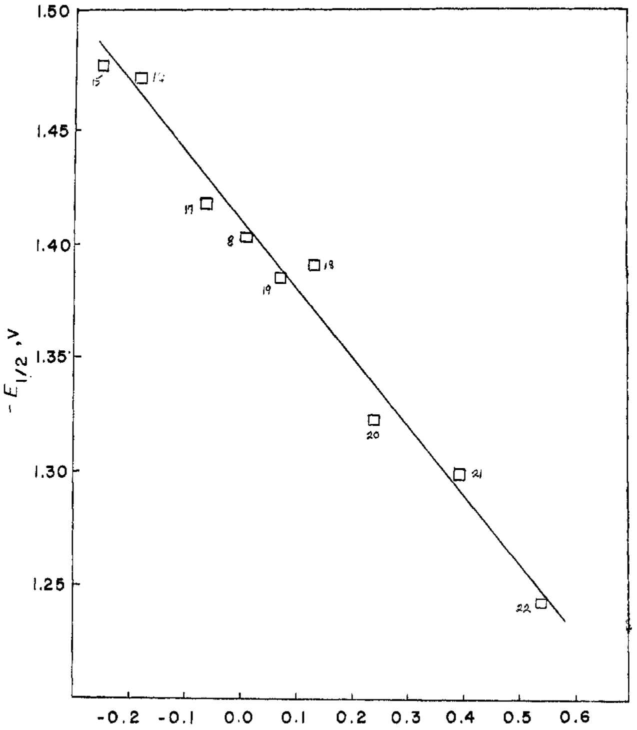


Figure 3.—Plot of $-E_{1/2}$ (V) *vs.* σ for ring B substituted compounds.

A values, correlating only slightly better than those of ring B, was observed for the reduction of chalcones in aqueous media (Table IV).[11]

TABLE IV

HALF-WAVE POTENTIALS OF CHALCONES SUBSTITUTED IN RING B

Compd	Substituent	$-E_{1/2}$, V	Slope[a]
15	4'-CH_3O	1.477	0.061
16	4'-CH_3	1.474	0.065
17	3'-CH_3	1.419	0.056
18	3'-CH_3O	1.396	0.057
19	4'-F	1.385	0.057
20	4'-Cl	1.328	0.060
21	3'-Br	1.305	0.050
22	4'-CF_3	1.247	0.066

[a] The slope of $-E$ (V) *vs.* log $[i/(i_d - i)]$.

Treatment of this data by the two-parameter approach of Swain and Lupton again results in a poorer correlation ($r = 0.934$) than was obtained with the simple Hammett expression. However, the pattern of behavior of substituents in the chalcone system is further complicated in this case since the correlation of ring B data is better than that of the ring A data using the Swain–Lupton approach (*cf.* ref 6b).

Conclusions

The Hammett expression correlates the chalcone polarographic data very well, whereas the Swain–Lupton approach is not so successful. In spite of the overall good description of a variety of chalcone linear free energy relationship data by the Hammett expression, the relationship of ring A to B continues to exhibit interesting vagaries which do not appear, as yet, to fall into a discernible pattern. These differing results probably arise from conformational effects which may be a function of the physical phenomenon or chemical reaction used as a probe, or from the solvent system employed and perhaps they may also be a function of the expression with which the data are correlated. It would be premature to discuss the relative significance of these factors until the results of other investigations are available. Additional studies of similar α,β-unsaturated ketones including systems in which conformational changes are restricted are under way.

Experimental Section

Chalcones.—The melting points were obtained with a Thomas-Hoover Uni-melt and are uncorrected. The analyses were performed by Atlantic Microlab, Inc., Atlanta, Ga. All chalcones were made following the procedure of Kohler.[24] The physical properties of all the chalcones shown in Tables I and II were described previously by us[6b] except **4**, **5**, and **22**. Compound **4** has been reported by Kostanecki and Schinder,[25] observed mp 61.5–62° (lit. mp 63°). Compounds **5** and **22** appear to be new. **5**: bp 179° (0.075 mm); λ_{max} 253 nm (ε 11,000), 300 (11,500), 350 (10,400). *Anal.* Calcd for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39. Found: C, 80.79; H, 6.50. **22**: mp 117.5–118.5°; λ_{max} 233 nm (ε 10,300), 318 (19,700). *Anal.* Calcd for $C_{16}H_{11}F_3O$: C, 69.59; H, 3.98. Found: C, 69.36; H, 4.17. The chalcones were purified and dried as previously reported.[6b]

Electrochemistry.—The dimethylformamide was purified by shaking over several portions of molecular sieves (Linde size 4A) followed by vacuum distillation. The middle 60% was collected and used on the day of the distillation. Tetraethylammonium perchlorate, used as the supporting electrolyte, was prepared according to the method of Kolthoff[26] and stored in an oven at 80° until used. Airco prepurified nitrogen was used for solution deaeration.

The polarograph consisted of a three-electrode potentiostat and ramp generator of conventional design.[14a] All polarograms were recorded on a Hewlett-Packard 7005-B x-y recorder. The polarographic scan rate was 0.06 V/min. For the cyclic experiments a fast-rise time potentiostat similar to one discussed in the literature[27] and a model 564 Techtronic scope were employed.

The polarographic cell consisted of a 100-ml Brezelius beaker fitted with a Teflon top into which the electrodes and gas dispersion tube were inserted. The reference electrode, an aqueous sce, was separated from the test solution by a bridge filled with DMF and TEAP. A platinum button was used as the auxiliary electrode. The open circuit capillary constant, $m^{2/3}t^{1/6}$, was 1.625. A Metrohm EA-410 microburet and EA-874 and EA-876-5 cells were used for the cyclic voltammetry experiments.

All glassware was carefully cleaned, then dried at 100–120° for several hours immediately prior to each experiment to ensure dryness.

The reported half-wave potentials are the average of at least nine polarograms taken on three separate days. The maximum range was 5 mV. The $E_{1/2}$ value of a given polarogram was the zero intercept of a plot of log $(i/i_d - i)$ *vs.* E. This intercept was determined by the least squares analysis of ten maximum currents taken from each side of a graphically approximated $E_{1/2}$.

Registry No.—**1**, 22965-98-6; **2**, 22252-15-9; **3**, 22965-99-7; **4**, 32111-71-0; **5**, 32111-72-1; **6**, 22252-14-8; **7**, 22966-01-4; **8**, 614-47-1; **9**, 22966-07-0; **10**, 22966-06-9; **11**, 22252-16-0; **12**, 22966-11-6; **13**, 22966-12-7; **14**, 22966-16-1; **15**, 22966-19-4; **16**, 14802-30-3; **17**, 13565-44-1; **18**, 22966-24-1; **19**, 22966-25-2; **20**, 22966-22-9; **21**, 22966-26-3; **22**, 32120-33-5; dimethylformamide, 68-12-2.

---

(24) E. P. Kohler and H. M. Chadwell, "Organic Syntheses," Collect. Vol. I, Wiley, New York, N. Y., 1932, p 78.

(25) St. V. Kostanecki and M. Schinder, *Ber.*, **29**, 1891 (1896).

(26) I. M. Kolthoff and J. F. Coetzee, *J. Amer. Chem. Soc.*, **86**, 3403 (1964).

(27) E. R. Brown and D. E. Smith, *Anal. Chem.*, **40**, 1411 (1968).