Bromination of 1,1-Diphenylethylenes. I. A Kinetic Study of Monosubstituted Derivatives in Methanol[1a]

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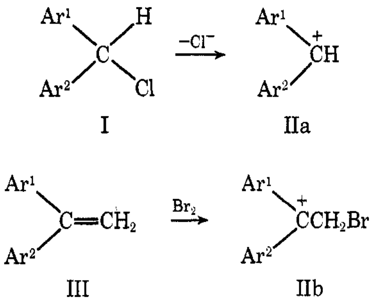
The kinetics of bromination of 11 meta- and para-substituted 1-aryl-1-phenylethylenes have been studied at 25° in methanol containing 0.2 M sodium bromide. The principal method used to study these rapid rates used an electrometric apparatus to maintain a constant low concentration of bromine in solution. Study of representative compounds showed that, under these conditions, molecular bromine was the only electrophilic species of importance. The rate constants for the meta-substituted compounds were correlated with $\rho = -3.57$ ($\log k_0 = 3.25$); this allowed the calculation of a coefficient for the transmission of resonance effects from the para position of the aryl ring of 0.84.

The reactivities of a large number of electrophilic side-chain reactions have been correlated using the unique set of σ^+ values of Brown and Okamoto.[2] However, Nishida[3] using more extensive data than previously available on the solvolysis of mono- and disubstituted benzhydryl chlorides (I) found that good correlations with σ^+ were only obtained when the substituent in one of the rings was varied, the other aryl ring being kept constant. Although simple additivity of substituent effects was observed in a limited number of cases,[3a,4,5] independent of their positions (meta or para) in either ring, in general it was concluded that the substituent effects were not additive (in the Hammett sense), not only when the two substituents were in different rings, but also when both were in the same ring.[3b]

This nonadditivity, where two substituents do not stabilize the transition state by the sum of the effects of the single substituents acting alone, appeared to be greatest when two substituents capable of electron donation by resonance were involved. However, whether this was due to saturation of resonance or the stereochemistry of the particular system chosen is not clear.


I IIa III IIb

The kinetic method involved in solvolysis is limiting in that only a narrow range of reactivity can accurately be measured under a given set of conditions, the other rate values being estimated from data obtained in different conditions or at different temperatures. On the other hand, the bromination of 1,1-diphenylethylenes (III), which we have used to generate much the same kind of intermediate (IIb) as involved in the solvolysis reaction (IIa), is not subject to the same limitations. The reaction is very rapid when electron-donating substituents are present (up to 10^6 l. mol^{-1} sec^{-1}), but rate constants of this order are readily accessible when low concentrations of the reactants are used.[6] We report here a study of the bromination of a large number of monosubstituted 1,1-diarylethylenes. Using these results we can then hopefully define a model system showing "normal" behavior, thus leading to the separation of electronic and stereochemical factors which might contribute to nonadditivity.

Results and Discussion

Brominating Agent.—The bromination of 11 monosubstituted 1,1-diphenylethylenes has been studied at 25° in methanol containing 0.20 M sodium bromide (Table I). Under these conditions, little free bromine remains in solution, most of it being converted to tribromide ion, since the equilibrium constant (K) for the formation of tribromide ion is 177.[7] Bromination, however, may now conceivably take place by either of the brominating agents, molecular bromine or tribromide ion. It is important to know the relative amounts of bromination that occur by each of these two

TABLE I

RATE CONSTANTS[a] FOR THE BROMINATION OF SUBSTITUTED 1,1-DIPHENYLETHYLENES, $XC_6H_4C(=CH_2)C_6H_5$, IN METHANOL AT 25°

Registry no.	Substituent X	k_{obsd}, l. mol^{-1} sec^{-1}
4333-75-9	*p*-MeO	3.76×10^6
948-55-0	*p*-Me	1.56×10^4
4333-70-4	*m*-Me	3.28×10^3
530-48-3	H	1.67×10^3
34564-79-9	*m*-MeO	1.64×10^3
395-21-1	*p*-F	1.33×10^3
18218-20-7	*p*-Cl	4.73×10^2
4333-76-0	*p*-Br	3.61×10^2
29265-80-3	*m*-F	9.00×10
29265-81-4	*m*-Cl	7.30×10
29265-84-7	*m*-NO_2	7.00

[a] Listed in order of decreasing reactivity.

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[1] (a) This paper may also be considered as part XXXI of the series "Olefinic Compounds Reactivity: Bromination." Part XXX: M. F. Ruasse and J. E. Dubois, *J. Org. Chem.*, **37**, 1770 (1972). (b) Chemistry Department, University College, Cork, Ireland. (c) 1851 Postdoctoral Fellow 1967–1968. (d) The Hebrew University of Jerusalem, Israel.

[2] H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **80**, 4979 (1958).

[3] (a) S. Nishida, *J. Org. Chem.*, **32**, 2692, 2695 (1967); (b) *ibid.*, 2697 (1967); (c) E. Berliner and M. Q. Malter, *J. Org. Chem.*, **33**, 2595 (1968).

[4] J. Packer, J. Vaughan, and A. F. Wilson, *J. Org. Chem.*, **23**, 1215 (1958).

[5] J. F. Kirsch, W. Clewell, and A. Simon, *ibid.*, **33**, 127 (1968).

[6] J. E. Dubois, *Z. Electrochem.*, **64**, 143 (1960).

[7] J. E. Dubois and H. Herzog, *Bull. Soc. Chim. Fr.*, 57 (1963).

species, since they would most likely have quite different responses to the variation of substituents in the aromatic rings.[8,9] Under these conditions, Bartlett and Tarbell[10] originally demonstrated that the overall expression (eq 1) is followed, where k_{obsd} is the observed

$$k_{obsd} = (\alpha + \beta[Br^-])/(1 + K[Br^-]) \qquad (1)$$

second-order rate constant at a given bromide ion concentration, and α and β are constants. This has more recently been confirmed to a high degree of accuracy in the bromination of *trans*-stilbene over almost the complete range of possible variation of the $(1 + K[Br^-])$ term.[11]

Although other explanations are possible for the terms α and β, these are usually associated with k_{Br_2} and $Kk_{Br_3^-}$, respectively, where k_{Br_2} is the specific rate constant for the bromination of the substrate by molecular bromine, $k_{Br_3^-}$ by tribromide ion. The α term is the least controversial, since, when $[Br^-] = 0$, then $k_{obsd} = k_{Br_2}$. This value is obtained by the extrapolation of a plot of $k_{obsd}\ (1 + k[Br^-])$ *vs.* Br^- to zero bromide ion concentration, rather than by the determination of the rate constant in the absence of bromide ion. This latter condition would involve indefinite and complex rate expressions, since the quantity of bromide ion increases as the reaction proceeds and would complex with the unreacted bromine. The $k_{Br_3^-}$ term (contained in β) may represent rate-determining reaction with an electrophilic, polarized Br_3^- species or alternatively, being kinetically indistinguishable, successive reaction by Br_2 and Br^- (in whatever order) with the substrate.[12] Recent evidence suggests, however, that both mechanistic pathways may operate;[13] there is good evidence from the change in product with bromide ion concentration that in the bromination of acetylenes the $k_{Br_3^-}$ term represents Br^--assisted attack of Br_2.[14] This latter mechanism is to be favored in those cases where Br_3^- is apparently a better electrophile than Br_2.

Although no simple relation, applicable to all substrates, between the relative efficiency of the two apparent brominating agents ($k_{Br_2}/k_{Br_3^-} = Q$) and the structure of the substrate is available,[15] there is a general decrease in the ratio (*i.e.*, Q tends toward unity and in some cases is actually less than unity[16]) as the reactivity of the olefin within a given series decreases.[9] The least reactive olefin, *viz.*, 1-(*m*-nitrophenyl)-1-phenylethylene, was therefore chosen for study in detail since the intervention of Br_3^- (or $Br_2 + Br^-$) would be most critical here, together with two compounds of intermediate reactivity (see Table II). In each case the bromination by tribromide ion is relatively unimportant despite its large concentration in solution. The effect of bromide ion was studied under conditions where the ionic strength was not maintained constant by the presence of another salt, mainly since previous attempts to nullify specific salt effects in bromination reactions have not been successful,[17] different slopes (β) of $k_{obsd}\ (1 + K[Br^-])$ *vs.* $\{Br^-\}$ being obtained with different inert salts. In the absence of another salt the extrapolated k_{Br_2} value is at least free from salt effects.

TABLE II

EFFECT OF BROMIDE ION CONCENTRATION ON THE RATE OF BROMINATION OF SOME 1,1-DIARYLETHYLENES IN METHANOL AT 25°

A. 1-(*m*-Nitrophenyl)-1-phenylethylene

$[Br^-]$	k_{obsd}	
0.05	20.3	
0.10	13.2	$k_{Br_2} = 188$
0.15	9.90	
0.20	7.05	$k_{Br_3^-} = 2.67$
0.25	7.00	$Q = 70$

B. 1,1-Di-*p*-fluorophenylethylene

$[Br^-]$	$10^{-3}k_{obsd}$, l. $mol^{-1}\ sec^{-1}$	
0.05	3.27	
0.10	1.95	$k_{Br_2} = 3.06 \times 10^4$
0.15	1.61	$k_{Br_3^-} = 3.66 \times 10^2$
0.20	1.23	$Q = 85$
0.25	3.92	

C. 1-(*p*-Fluorophenyl)-1-phenylethylene

$[Br^-]$	$10^{-3}k_{odsd}$, l. $mol^{-1}\ sec^{-1}$	
0.05	3.92	
0.10	2.19	$k_{Br_2} = 3.16 \times 10^4$
0.15	1.63	$k_{Br_3^-} = 5.57 \times 10^2$
0.20	1.33	
0.25	1.30	$Q = 57$

The confidence limits of the utilization of k_{obsd} in place of the k_{Br_2} value in the estimation of linear free energy relationships have been mathematically calculated.[18] With Q greater than 50 (that is, $k_{Br_3^-}$ tending toward zero, as we have found), essentially the same results are obtained using either k_{obsd} or k_{Br_2}. This being the case, we have used the k_{obsd} value throughout in the evaluation of the rate data.[19] It is not possible to comment on the small variation of Q with structure, since values as large as this are very sensitive $\{$as the slope of the plot of $(1 + K[Br^-])$ *vs.* Br^- plot nears zero$\}$ to the experimental error involved in measuring k_{obsd}; the final error in Q in the values quoted is therefore *ca.* ±20%, even though the k_{obsd} values are accurate to 3%.

Substituent Effects.—To establish unequivocally the true ρ value for the bromination of 1,1-diphenylethylenes, five meta-substituted compounds were chosen. Only the data for 1-(*m*-methoxyphenyl)-1-phenylethylene were omitted, since the σ_m^+ value for the *m*-MeO substituent has not been well established and may be variable in electrophilic reactions.[20] An excellent correlation was obtained with $\rho = -3.572$, $r = 0.999$, $s = 0.0047$, and $\log k_0 = 3.25$. It is clearly seen from

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[8] J. E. Dubois and J. J. Aaron, *J. Chim. Phys.*, 1354 (1964).

[9] J. H. Rolston and K. Yates, *J. Amer. Chem. Soc.*, **91**, 1469, 1477, 1483 (1969).

[10] P. D. Bartlett and D. S. Tarbell, *ibid.*, **58**, 466 (1936).

[11] J. E. Dubois and F. Garnier *Bull. Soc. Chim. Fr.*, 4512 (1967).

[12] R. P. Bell and M. Pring, *J. Chem. Soc. B*, 1119 (1966).

[13] J. E. Dubois and X. Q. Huynh, *Tetrahedron Lett.*, 3369 (1971).

[14] J. A. Pincock and K. Yates, *Can. J. Chem.*, **48**, 3332 (1970); *J. Amer. Chem. Soc.*, **90**, 5643 (1968).

[15] E. Bienvenue-Goetz, D.Sc. Thesis, University of Paris, 1967; A. F. Hegarty and F. L. Scott, *J. Chem. Soc. B*, 1031 (1966).

[16] N. P. Kanyaev, *J. Gen. Chem. USSR*, **26**, 3037 (1956); **29**, 825 (1959).

[17] R. P. Bell and D. J. Rawlinson, *J. Chem. Soc.*, 63 (1961).

[18] J. E. Dubois and X. Q. Huyhn, *Bull. Soc. Chim. Fr.*, 1436 (1968).

[19] In any event, the composite rate constant k_{obsd}, without the separation of the individual contributions due to Br_2 and Br_3^-, has been successfully used in many cases in studying the effect of molecular structure on reactivity; see, *e.g.*, J. E. Dubois and G. Mouvier, *Tetrahedron Lett.*, 1325 (1963); A. F. Hegarty and F. L. Scott, *J. Chem. Soc. B*, 672 (1966).

[20] Use of the σ_m^+ value of +0.048, given by Brown and Okamoto[2] for methoxy, does not disimprove the correlation.

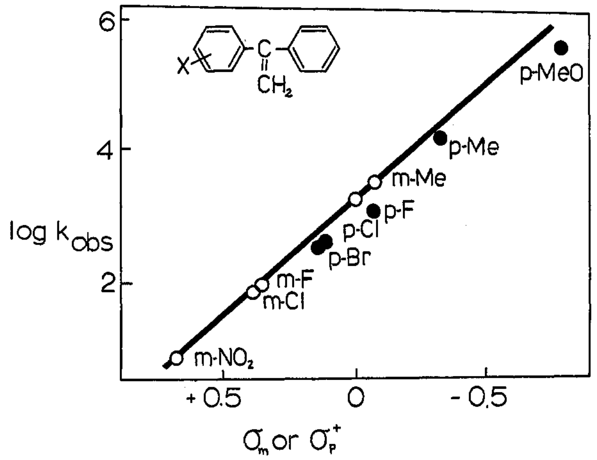

Figure 1.—Hammett plot of log k for the bromination of $Ar(Ph)C = CH_2$ *vs.* σ for meta-substituted compounds (○) and σ^+ for para-substituted compound (●), showing the overcorrelation for resonance involved in using the σ^+ values of Brown and Okamoto.[2]

Figure 1 that Brown and Okamoto's[2] σ^+ values place the kinetic data for all the para-substituted ethylenes *below* this line. This implies that resonance interactions between the substituents and the reaction center are somewhat less than in the defining reaction for σ^+. We have therefore applied the Yukawa–Tsuno equation[21] to the data for the para-substituted ethylenes in the form

$$\log k = -3.57(\sigma_0 + R\Delta\sigma^+) + 3.25$$

using the ρ value of −3.57 previously obtained from meta substituents. A least-squares treatment of the data for the five para-substituted 1,1-diphenylethylenes gave the resonance susceptibility constant, R = 0.84 (with r = 0.993, s = 0.019).[22] This value is remarkably close to that already reported (0.81) for substituent effects (by electron-donating substituents) on the pmr chemical shifts of the ethylenic proton of diphenylethylenes.[23]

The magnitude of R has been shown to decrease when the angle of rotation, ϕ, between the phenyl ring and the plane of the ethylenic bond is increased (resulting from decreased orbital overlap).[24] However, an estimate of the configuration of the molecule in the transition state can only be made if a reliable model is available for the situation when $\phi = 0°$. If, as an approximation, it is assumed that this condition is met in the solvolysis of cumyl chlorides where R = 1.0,[2] then the R of 0.84 obtained in the present instance implies that ϕ = *ca.* 23° (if the susceptibility constant varies with $\cos^2 \phi$).[25]

The ρ value obtained is lower than that reported by Nishida[3a] for the corresponding nonsubstituted benzhydryl chlorides (−4.22), also in methanol at 25°, or the bromination of meta- and para-substituted styrenes under the same conditions (−4.30).[26] However, the bromination of diphenylethylenes involves a transition state in which there is partial formation of a tertiary carbonium ion (IIb), whereas the solvolyses or the styrene bromination result in secondary carbonium ions (see IIa). The ρ value is found generally to decrease as the carbonium ion is successively primary, secondary, and tertiary; *e.g.*, the solvolysis of triphenylmethyl chloride in 40:60 ethanol–diethyl ether has a ρ of −2.34.[27] Moreover, any deviation from an open carbonium ion structure due to the participation of bromine as a neighboring group, although unlikely on the evidence for the bromination of styrenes,[9,28] would tend to reduce the sensitivity of the reaction to substituent effects. Also, any bromination by tribromide ion, although it has been shown to be an unimportant electrophilic species in the present study, would tend to reduce rather than increase the magnitude of the ρ value.[9,14]

Experimental Section

The 1,1-diarylethylenes were synthesized mainly using the Grignard reaction, either between the corresponding benzophenones and methylmagnesium iodide or between suitable acetophenones and arylmagnesium halides. The method is not applicable to the preparation of nitro-substituted 1,1-diarylethylenes. The Wittig reaction between nitrobenzophenone and triphenylphosphine–methylene gives generally very low yields, but Horner's modification of the Wittig reaction,[29] using triethyl phosphonoacetate, proved to be the only method of choice. The ester so obtained was not only hydrolyzed but also directly decarboxylated, when it was treated with a mixture of sulfuric and acetic acids.

Many of the compounds used in this study have been described previously.[30] The properties of the new substances are listed in Table III; in the following two representative syntheses are described.

TABLE III

ANALYTICAL AND PHYSICAL DATA FOR THE MONOSUBSTITUTED 1,1-DIPHENYLETHYLENES

$XC_6H_4C(=CH_2)C_6H_5$

X	Bp, °C (mm)	Yield, %
3-Me[a]	162 (18)	53
3-MeO[b]	185–187 (27)	64
3-NO_2[a]	146 (0.5)	25
3-F[a]	153–154 (22)	40
3-Cl[a]	185–187 (30)	31

[a] Satisfactory combustion analytical data (±0.3%) were provided for these compounds: Ed. [b] Calcd: C, 85.68; H, 6.71; MeO, 14.82. Found: C, 86.12; H, 6.70; MeO, 15.01.

1-(*m*-Tolyl)-1-phenylethylene.—To the solution prepared from *m*-bromotoluene (8.6 g) and magnesium (1.21 g) in anhydrous ether (50 ml), acetophenone (6.0 g) in ether (10 ml) was added slowly. The solution was refluxed for 2 hr and decomposed with 6 *N* hydrochloric acid (60 ml). Two distillations gave 5.6 g of the *ethylene*, bp 162° (18 mm). If dehydration did not occur spontaneously in the first distillation, a few crystals of iodine

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[21] Y. Yukawa and Y. Tsuno, *J. Chem. Soc. Jap.*, **86**, 875 (1965); we use R rather than r for the resonance susceptibility constant, to avoid confusion with the correlation coefficient.

[22] This again demonstrates how many reactions appear to be well correlated by σ^+ values whereas in reality the use of the Yukawa–Tsuno equation on the basis of meta-substituted compounds to establish ρ gives an R value of 1.0 ± 0.3 [see, for example, P. R. Wells, *Chem. Rev.*, **63**, 171 (1963)]; part of the variation in σ is absorbed by the ρ value. In the present instance, use of σ^+ values for the ten substituted ethylenes gives a good fit (r = 0.996, s = 0.118), but the ρ value at −3.24 is significantly lower.

[23] Y. Yukawa, Y. Tsuno, and H. Yamada, *Mem. Inst. Sci. Ind. Res. Osaka Univ.*, **23**, 79 (1966).

[24] J. E. Dubois and A. F. Hegarty, *J. Chem. Soc. B*, 638 (1969).

[25] A. F. Hegarty and J. E. Dubois, *Tetrahedron Lett.*, 4839 (1968).

[26] J. E. Dubois and A. Schwarz, *ibid.*, 2167 (1964).

[27] A. C. Nixon and G. E. K. Branch, *J. Amer. Chem. Soc.*, **58**, 492 (1936).

[28] R. C. Fahey and H. J. Schneider, *ibid.*, **90**, 4429 (1968).

[29] L. Horner, H. Hoffmann, and H. G. Wippel, *Chem. Ber.*, **91**, 61 (1958); L. Horner, H. Hoffmann, H. G. Wippel, and G. Klahre, *ibid.*, **92**, 2499 (1959).

[30] F. Bergmann and J. Szmuszkovicz, *J. Amer. Chem. Soc.*, **70**, 2748 (1948); E. D. Bergmann and A. Bondi, *Chem. Ber.*, **63**, 1158 (1930); **64**, 1455 (1931).

were added and the product was redistilled. The distillate was then diluted with ether, washed free of any remaining iodine with an aqueous sodium thiosulfate solution, dried, and redistilled.

1-(*m*-Nitrophenyl)-1-phenylethylene.—In an atmosphere of dry nitrogen, triethyl phosphonoacetate (10 g) was added slowly to a suspension of sodium hydride (1.0 g) in 80 ml of dry dimethylformamide so that the temperature remained below 20°. After 1 hr at ambient temperature, *m*-nitrobenzophenone (10 g) was added and the mixture was heated, with vigorous stirring, at 120° for 4 hr. The mixture was then poured into 2 l. of cold water and the organic product was extracted with chloroform. The chloroform extract was washed (with water and then with concentrated sodium carbonate solution) and concentrated, and the residue was refluxed for 5 hr with glacial acetic acid (100 ml) and 10% sulfuric acid (80 ml). The solution was poured into 2 l. of cold water and the product was reextracted with chloroform. After washing (as before) and drying, distillation, bp 146° (0.5 mm), gave the olefin as a yellow solid. Several crystallizations from hexane gave 2.5 g of pure 1-(*m*-nitrophenyl)-1-phenylethylene, mp 82.5°.

In all cases the olefins were stored under nitrogen before use to minimize oxidation to the corresponding diaryl ketones. Even under these conditions, some oxidation took place; shortly before a kinetic run, the olefins were purified by vapor phase chromatography using an Aerograph Model 600-C chromatograph, with a 10-ft SE-30 column at 165–175°. All of the substrates thus obtained and used in the kinetic studies were greater than 99.5% pure. The purity of the substrates is, however, not critical when the concentrostat (see below) is used, provided that the impurities are brominated either much more rapidly or slowly than the olefin under study. Since the concentrostat employs a pseudo-constant concentration of bromine, the reaction is first order in (and therefore independent of the initial concentration of) the olefin.

Kinetic Measurements.—All kinetic experiments were at 25.0 ± 0.1° in methanol containing 0.20 *M* sodium bromide (unless otherwise stated). The methanol was reagent grade, treated as follows. Bromine (3–4 drops per liter) was added and, after standing overnight, the methanol was fractionated, the middle portion (50% of total) being retained. The distillate was similarly treated and redistilled; a final distillation from potassium carbonate removed small traces of hydrogen bromide formed. The methanol thus obtained contained less than 0.05% water (Karl–Fischer titration) and did not react significantly with bromine. No correction had to be made for the reaction of bromine with the solvent in a kinetic experiment if the time of reaction (10 half-lives) was less than 1 hr (and this was generally the case). The sodium bromide (Prolabo R. P. grade) was dried at 120° overnight before use.

Three electrometric methods were used to measure the rate constants which were all in the region 1–10^7 l. mol^{-1} sec^{-1}. The actual method used for a given compound depended on its rate constant, since each method had an optimum region of operation, namely (1) potentiometric, 1–10^4 l. mol^{-1} sec^{-1}; (2) concentrostat, 10^2–10^5 l. mol^{-1} sec^{-1}; (3) amperometric, $>10^4$ l. mol^{-1} sec^{-1}. These barriers are not precise, however, and many compounds could be studied using more than one method. When this was possible, the various methods gave concordant results within the experimental errors listed. Each kinetic experiment was repeated a *minimum* of five times (and in many cases up to ten times), using various initial concentrations of olefin and bromine. The actual experimental errors, which varied with the magnitude of the rate constants, were as follows: $k > 10^4$, standard deviation 2%; $10^4 < k < 10^6$, 3%; $k > 10^6$, 4%. The calibration of the various apparatus was checked periodically using as standards compounds whose rate constants are well established, *e.g.*, cyclohexene,[31] $k_2 = 790$ l. mol^{-1} sec^{-1}, and allyl alcohol,[32] $k_2 = 4.73$ l. mol^{-1} sec^{-1}.

(1) The potentiometric method was essentially that used extensively by Bell and coworkers,[33] with the following modifications. A silver–silver chloride reference electrode (connected to the cell by a salt bridge containing a saturated methanolic solution of sodium bromide) was used with the platinum indicating electrode, and a Honeywell Model 1508 Visicorder was used to record the potential difference between these electrodes. Bromine was introduced coulometrically using Metrohm smooth platinum electrodes, the cathode being separated from the reaction solution by a fritted glass disk. The rate constant is given by

$$k_2 = -78.2 \frac{\mathrm{d}E/\mathrm{d}t}{c}$$

where c is the olefin concentration and E is the potential difference (in volts) between the electrodes. The olefin was in at least a 20-fold excess, so that c is approximately constant; the rate constants were obtained directly from the resultant linear voltage–time plots. Changes in potential of 60 mV were followed representing >95% bromine reacted.

(2) The concentrostat, developed by Dubois and coworkers,[34] employs a constant concentration of bromine (*ca.* 10^{-5}–10^{-6} *M*) so that the reaction becomes pseudo-first-order in olefin. The cell, with a volume of 100 ml and thermostatted at 25°, contained three pairs of platinum electrodes, a thermometer, sample inlet, and stirrer. The bromine generation electrodes consisted of a platinum gauze (2 cm^2) anode in the reaction solution and a spiral platinum wire electrode (6 cm long, 1-mm diameter) in a second compartment containing a saturated methanolic solution of sodium bromide and separated from the reaction solution by a fritted glass disk. The bromine was generated using a pulse coulometer constructed in the laboratory (each pulse 0.12 sec duration) with currents varying from 3 to 60 mA depending on the constant bromine concentration required (which, in turn, was dependent on the rate constant being measured; higher bromine concentrations were used with slower reactions). To regulate the frequency of the pulses so that a constant bromine concentration was maintained as the bromine reacted with the olefin, two further electrodes (identical, each 2 cm long, 0.25 mm diameter) were dipped in the reaction solution. These were polarized by 0.6–4.6 V (the most sensitive position was sought) and connected to the concentrostat, which essentially regulated the bromine generation electrolysis current to maintain the current in the second circuit (and thus the bromine concentration) at the constant predetermined value. Typically, when 100 ml of the solvent had been introduced and the temperature had equilibrated, sufficient bromine was generated rapidly by electrolysis to give a final k_1 in the region 3×10^{-3} to 1.5×10^{-2} sec^{-1} (see below). The olefin was then added from a syringe, and the bromine was automatically maintained constant by the electrolysis current. After several such dry runs to optimize the reaction conditions and to condition the cell and electrodes to the substrate and reaction products, the total electrolysis time (*i.e.*, the number of current pulses multiplied by their duration) was plotted against the elapsed time using a printed read-out on a Hewlett-Packard Model H23563-A Digital Recorder.

Since the bromine concentration remains constant, a plot of the integrated electrolysis time (θ) against the elapsed time (t) gives the relation from which the rate constant with respect to the olefin is found.

$$k_1 = 2.303 \log \frac{(\theta_\infty - \theta_t)}{t}$$

θ_∞ is the calculated electrolysis time when $t = \infty$ which best fitted the relationship; this was invariably within 1% of the observed value. The observed second-order rate constant $k_2 = k_1/[\text{Br}_2^*]$. The constant bromine concentration ($\text{Br}_2^* = \text{Br}_2 + \text{Br}_3^-$) was determined amperometrically in the cell using the third pair of electrodes which were identical to the second pair but polarized by 0.2 V. An excess of arsenic acid solution was added, and the excess was determined titrimetrically against bromine. Finally the arsenic acid solution was standardized, also by titration against electrogenerated bromine.

(3) The coulometric apparatus, in which the limiting diffusion current of bromine at a rotating platinum electrode is measured as a function of time, has previously been described.[35] The exact initial bromine and olefin concentrations were determined by calibrating the recorder deflection each time using electrogenerated bromine; usually a bromine–olefin ratio of approximately 2:1 was used in these kinetic experiments.

Although no detailed product analysis was carried out in the present work, it has been shown that the bromination in benzene

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[31] J. E. Dubois, M. Ropars, and P. Fresnet, *J. Chim. Phys.*, 856 (1965).

[32] J. E. Dubois and E. Goetz, *Tetrahedron Lett.*, 303 (1965).

[33] R. P. Bell and D. Dolmann, *J. Chem. Soc. B*, 500 (1968).

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or chloroform solution, even of the most reactive substrates studied, *viz.*, 1-(*p*-methoxyphenyl)-1-phenylethylene, gives substitution products, *e.g.*, 1,1-diphenyl-2-bromoethylene from 1,1-diphenylethylene, in high yield.[36] In the methanolic solvent used in the present study, some solvent attack (giving methoxy bromo products) is conceivable, but would not alter the observed kinetics or conclusions. Dibromination, either at the 1 position or in the aromatic ring, was not apparent in any case (all the reactants followed clean second-order kinetics); moreover, the 2-bromo substituent (in the product) deactivated the olefin greatly to electrophilic attack; 2-bromo-1,1-diphenylethylene was brominated under the conditions used to study the kinetics approximately 10^5 times less rapidly than the parent 1,1-diphenylethylene.

Registry No.—1,1-Di-*p*-fluorophenylethylene, 6175-14-0.

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Bromination of 1,1-Diphenylethylenes. II. Resonance Saturation and Geometrical Effects on the Reactivity of Multiply Substituted Derivatives[1,2]

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The substituent effects for multiple substitution on the kinetics of bromination of 1,1-diarylethylenes are not additive and exhibit apparent saturation of π-electron resonance stabilization. The majority of the rate constants can, however, be correlated, using a single reaction constant, by the linear parametric equation $\log k/k_0 = \rho(\sigma^+ + \sigma)$, with $\rho = -3.26$ and $\log k_0 = 3.169$. This is tantamount to postulating an unsymmetrical transition state in which one of the aryl rings remains planar and conjugated with the developing carbonium ion, the other ring (of necessity due to steric restriction) lying out of this plane. This equation is rigorously tested with 32 meta- and para-substituted diarylethylenes varying in reactivity by 7 powers of 10 (in MeOH at 25°). An alternative transition state in which both aryl rings are equally inclined to the plane of the carbonium ion proves less exact. A more detailed treatment, to include data for compounds which deviate from the above modified Hammett equation, requires that the presence of a substituent in one of the aryl rings also changes the ρ value for substituent variation in the second ring. The varying ρ's thus obtained for the bromination of 1-(substituted phenyl)-1-arylethylenes are -2.27 (substituent = *p*-MeO); -3.03 (*p*-Me); -3.57 (H); -3.67 (*p*-Br); -3.42 (*m*-Me); -3.69 (*m*-MeO); -4.08 (*m*-Cl); -4.65 (*m*-NO$_2$). The ρ values are proportional to the σ^+ of the substituent which is held constant. A similar multiple ρ treatment is found also to be applicable to data for the solvolysis of benzhydryl chlorides.

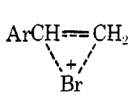
Recent studies by Yates and Rolston[4,5] and by Fahey and Schneider[6] have conclusively demonstrated that the electrophilic bromination of styrene derivatives I involves open benzylic-type carbonium ions II rather than cyclic bromonium ion intermediates III, as had previously been supposed. Thus bromination of *cis*- and *trans*-1-phenylpropene (IV) is nonstereoselective, both in carbon tetrachloride[6] and acetic acid solvents,[4] although the trans adduct is favored under most conditions. In acetic acid, solvent attack gives exclusively 1-acetoxy-2-bromo (V), rather than 1-bromo-2-acetoxy, products.[4] Kinetic evidence also supports this conclusion, since the ρ values for the bromination of styrenes (-4.21 in acetic acid[5] and -4.30 in methanol)[7] are comparable to those commonly reported for α-phenylcarbonium ion formation (as in the solvolysis of carbinyl chlorides, where $\rho = -4.54$.)[8] Similar evidence has been presented[9] to support the existence of open-chain vinyl cationic species in the bromination of phenyl acetylenes.

ArCH=CH$_2$

I

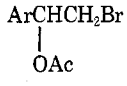

$\mathrm{Ar\overset{+}{C}HCH_2Br}$

II

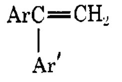

III

C$_6$H$_5$CH=CHCH$_3$

IV


$\mathrm{ArCH(OAc)CH_2Br}$

V


$\mathrm{ArC(Ar')=CH_2}$

VI

This polarization of charge in the transition state would be expected to be far greater in the bromination of 1,1-diarylethylenes (VI). However, the rate enhancement reported on the introduction of one phenyl ring at the double bond (*i.e.*, styrene *vs.* ethylene) is greater (130-fold) than that for the introduction of the second aryl ring: 1,1-diphenylethylene is brominated only *ca.* 25 times more rapidly than styrene.[10] Clearly, part of this difference is due to the inability of the two aryl rings to be simultaneously coplanar with the double bond in VI (or in the carbonium ion formed from VI, which would have a similar sp^2 hybridized carbon center). However, the overall effect is an apparent "saturation" of resonance stabilization by the phenyl ring. Most reported cases of such saturation also involve substituents placed in such di- or triarylcarbonium ions[11-13] or carbanions.[14] It is of interest therefore to examine diphenylethylenes in which both aryl rings are substituted to discover whether simple geometric effects

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