

If it can be applied equally to the dimethylsulfonio group, then smaller groups such as dibromo and dichloro groups would be certainly less effective in blocking coplanarity of the particular group, even though Stuart models definitely indicate effective hindrance by dibromo groups. This would at least be in accord with our observation that, whereas two *o*-chlorine or bromine atoms have no influence on the acidifying effect of the *p*-dimethylsulfonic group in phenol, one *o*-methyl

group^{5b} had a definite if small influence in diminishing conjugation.

The ultraviolet spectra of both 3,5-dihalo-4-dimethylsulfoniophenols in neutral solution are the same as those in alkaline solution. Since both phenols are quite strong acids even in neutral solution they evidently dissociate to an appreciable extent, giving the absorption bands characteristic of phenolate. This dissociation was suppressed by addition of hydrochloric acid.

PHILADELPHIA 4, PENNA.

[CONTRIBUTION FROM THE DEPARTMENT OF GENERAL CHEMISTRY OF THE UNIVERSITY OF ROME]

The ρ - σ^+ Treatment for the Bromination of Substituted Polymethylbenzenes. The Kinetic Effect of the Cyano Group¹

BY GABRIELLO ILLUMINATI

RECEIVED JANUARY 14, 1958

The relative bromination rates of fluorobromomesitylene, cyanomesitylene and cyanodurene have been measured in nitromethane solution at 30°. A least square value of -8.690 for the reaction constant has been calculated from most *meta* reactivity data available for the present approach. Substituent σ_p^+ constants have then been evaluated and found to be in excellent agreement with Brown and Okamoto's constants. Surprisingly, a discrepancy is observed for the *m*-cyano group. The present data indicate similar values for the σ_m^+ and σ_p^+ constants of the cyano group: the possible link of such data with the orienting effect of this group in bromination with Br_2 is discussed.

In a previous paper,² we have shown that the electrical effects of halogens in such overcrowded molecules as halo tri- and tetramethylbenzenes are transmitted to a *meta* or *para* reaction center, on nuclear attack by molecular bromine, without appreciable steric disturbances. Furthermore, anticipation of some of Brown and Okamoto's results on their stimulating ρ - σ^+ treatment³ of aromatic substitution permitted a preliminary test, which turned out to be quite successful, of the σ^+ constants on our data and a graphical estimation of the reaction constant for bromination.

Our studies on the orientation effects of substituents by what it may be called, for brevity, the "polymethylbenzene approach" to the problem may be considered valuable in the following ways: (1) in the determination of the electrical effects of *m*- and *p*-substituents causing negligible steric interaction; and (2) in the estimation of steric effects in the case of substituents susceptible to deviation from co-planarity with the benzene ring and/or provided with much too large effective sizes.

We wish to treat the first point in this paper by extending the investigations to fluorobromomesitylene, cyanomesitylene and cyanodurene and by broadening the reactivity range from *p*-methyl⁴ to $\Sigma(m\text{-F}, m\text{-Br})$.

Substituents expected to give rise to steric effects, such as the *p*-nitro and *p*-methoxy groups,

because of their lower symmetry, will be dealt with in subsequent papers.⁵

Results

Since the reactivities relative to the parent hydrocarbon in the two *m*-polymethylbenzene series, those of mesitylene and isodurene, correspond to each other within a small factor, the *m*-cyano group was only examined in the former series for convenience. The initial rates for cyano- and fluorobromomesitylene and cyanodurene were measured in 0.055 *M* nitromethane solution and the rates relative to durene (=1000) calculated with the aid of chloromesitylene as the compound of intermediate reactivity. The new kinetic data are reported in Table I. The concentrations used in this work were made relatively high in order to compensate for the low reactivity of the compounds investigated, particularly cyanodurene. For the latter compound, autocatalytic phenomena began to appear as early as 10% changes or even less. Thus the extent of reaction used for the determination of the times at 10% reaction (t_{10}) was carefully chosen in each kinetic run and, whenever necessary, the t_{10} values were obtained by extrapolation (see Experimental). Residual superimposition of concurrent reactions might lead to an apparent relative reactivity (k/k_0) higher than the correct value by a supposedly small factor. Complications of this kind were not observed for cyano and fluorobromomesitylene, for which the reliability of the specific effects of the substituents involved finds a perfect correspondence in chlorination studies in acetic acid solution.⁶

(1) This paper is part VIII in the series "Substitution in Polymethylbenzenes"; preceding paper, G. Illuminati, *Nature*, **179**, 780 (1957).

(2) G. Illuminati and G. Marino, *THIS JOURNAL*, **78**, 4975 (1956).

(3) (a) H. C. Brown and Y. Okamoto, *ibid.*, **79**, 1913 (1957); (b) Y. Okamoto and H. C. Brown, *J. Org. Chem.*, **22**, 485 (1957).

(4) G. Illuminati, *Ric. Sci.*, **26**, 2752 (1956).

(5) For the *p*-methoxy group and other group VIb substituents, see G. Illuminati, *THIS JOURNAL*, **80**, 4945 (1958).

(6) E. Baciocchi and G. Illuminati, *Ric. Sci.*, **28**, 1159 (1958); part X.

TABLE I
KINETIC DATA ON THE BROMINATION OF SOME SUBSTITUTED
POLYMETHYLBENZENES IN 0.055 M NITROMETHANE SOLU-
TION, AT 30.0°

Aromatic compound	Substituent examined	t_{10}^a , min.	R^b	$10^3 \times (k/k_0)^c$
2-Fluoro-4-bromomesitylene	$\Sigma(m-F, m-Br)$	3,375	6.104×10^{-3} 6.938×10^{-3}	0.3115
2-Cyanomesitylene	$m-CN$	604	3.411×10^{-3} 3.877×10^{-3}	0.8704
3-Cyanodurene	$p-CN$	14,200	1.451×10^{-3} 1.647×10^{-3}	3.099
2-Chloromesitylene ^d		1.0	20.6 ^d	

^a Time at 10% reaction; mean from several determinations. ^b Rate relative to durene (= 1000). In the pairs of values given below for each compound, the second value was obtained with the aid of determinations on compounds of intermediate reactivity in 0.035 solution (unpublished studies). ^c Reactivity per position of attack relative to the parent hydrocarbon. All reported values were calculated from the mean R value. ^d For this value see ref. 2, Table I. ^e Reference compound.

In view of the success⁷ of the polymethylbenzene approach in correlating reactivity to structure, it will be noted that the method of measuring times at 10% reaction, which is the only one available to establish relative rates in aromatic bromination,⁸ yields sufficiently precise information despite possible fluctuations in the factors contributing to the kinetic form of this reaction.⁹ This becomes especially true when the investigated reactivities cover a many-power range.

Discussion

The Reaction Constant.—The study of the extension of the Hammett equation in the form³

$$\log(k/k_0) = \rho\sigma^+ \quad (1)$$

can be based soundly on Brown and Okamoto's criterion of correlating reactivity data with side-chain σ_m constants. The polymethylbenzene approach offers an opportunity to apply this criterion to typical aromatic substitutions, such as bromination, because it enables the determination of reliable *meta* reactivity data for *o,p*-orienting substituents.

The reliability of the reaction constant is subject to the reliability of the σ_m constants and to the validity of the assumption $\sigma_m^+ = \sigma_m$. Both such conditions appear to be met most satisfactorily with such substituents as the methyl group and the halogens.^{3,10} Accordingly, because of some uncertainties in the choice of the σ -constant for the *m*-cyano group, we have not included it in the calculations.

The reaction constant for the bromination of polymethylbenzenes was computed by least square methods¹¹ with the numerical data reported in Table II. The data involve 12 points and cover a reactivity range of 10^7 . The ρ -value thus found is

(7) Cf. ref. 2 and following section.

(8) P. W. Robertson, P. B. D. de la Mare and W. T. G. Johnston, *J. Chem. Soc.*, 276 (1943); E. Berliner and F. Berliner, *THIS JOURNAL*, **71**, 1195 (1949); P. B. D. de la Mare and C. A. Vernon, *J. Chem. Soc.*, 1764 (1951); G. Illuminati and G. Marino, ref. 2; H. C. Brown and L. M. Stock, *THIS JOURNAL*, **79**, 1421 (1957).

(9) R. M. Keefer and L. J. Andrews, *ibid.*, **78**, 3637 (1956); see, especially, p. 3639 for the criticisms on this method.

(10) H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

(11) See the appendix in ref. 10.

—8.690, in close agreement with a previous graphical evaluation (—8.64) including *m*- and *p*-reactivity data for the halogens²; also, the correlation is illustrated in Fig. 1, the correlation coefficient being 0.994 and the standard deviation 0.225.

TABLE II
meta REACTIVITY DATA USED FOR THE EVALUATION OF THE
REACTION CONSTANT

Aromatic compound	Substituent examined	$\log(k/k_0)$	Reference	σ_m or $\Sigma\sigma_m$
2-Fluoro-4-bromomesitylene	$\Sigma(m-F, m-Br)$	-6.506	This work	0.728
2-Fluoromesitylene	<i>m-F</i>	-3.068	2	.337
4-Fluoroisodurene	<i>m-F</i>	-2.914	2	.337
2-Chloromesitylene	<i>m-Cl</i>	-3.307	2	.373
4-Chloroisodurene	<i>m-Cl</i>	-3.192	2	.373
2-Bromomesitylene	<i>m-Br</i>	-3.361	2	.391
4-Bromoisodurene	<i>m-Br</i>	-3.202	2	.391
2-Iodomesitylene	<i>m-I</i>	-2.947	2	.352
4-Iodoisodurene ^a	<i>m-I</i>	-2.480	2	.352
2-Methylmesitylene (isodurene)	<i>m-CH₃</i>	0.433	2, 4	-.069
4-Methylisodurene (pentamethylbenzene)	<i>m-CH₃</i>	0.674	4 ^b	-.069

^a The k/k_0 value for this compound is higher than that for iodomesitylene by a factor of *ca.* 3, whereas the k/k_0 value for a substituted isodurene compound is, in the average, higher than that for the corresponding mesitylene compound by a factor of 1.5. The discrepancy may have an experimental origin as iodoisodurene was found to be an unstable compound over a period of months. ^b See, also, P. B. D. de la Mare and P. W. Robertson, *J. Chem. Soc.*, 279 (1943).

It is not yet possible to make a proper comparison of the ρ -constant for the bromination of polymethylbenzenes with that for the bromination of monosubstituted benzenes^{3,12} because of the lack of a sufficient amount of quantitative data in the latter case and of the difficulties¹³ in obtaining information on *meta* reactivity data with *para* orienting groups. Thus, the value of -11.35, as computed for "halogenation,"³ suffers from inclusion of chlorination data and from consideration of *p*-substituents only and, therefore, was intended as a tentative one. The available indications, however, make it likely that the magnitude of the bromination constant is indeed lower in the case of substituted polymethylbenzenes than in the case of monosubstituted benzenes.¹⁴ Such a difference probably should be sought in factors other than a mere effect of the number of methyl groups around the aromatic ring, otherwise the mesitylene series would not fit so well into the tetramethylbenzene lines. Undoubtedly, a common structural feature for all three series considered is, unlike monosubstituted benzenes, the presence of two methyl groups *ortho* to the reaction center and this may be a possible factor responsible for a separate ρ -value.

The σ^+ Constants.—The reaction constant and the remaining available data for the bromination of substituted polymethylbenzenes can now be used to evaluate an independent set of σ^+ values for the *p*-methyl, *m*- and *p*-cyano groups and the *p*-halogens. These constants are reported in Table III and compared with Brown and Okamoto's

(12) J. Miller, *Austr. J. Chem.*, **9**, 61 (1956).

(13) P. B. D. de la Mare, *J. Chem. Soc.*, 4450 (1954); see, especially, p. 4452.

(14) This would also appear from the chlorination reaction; see, in this connection, ref. 6 and H. C. Brown and L. M. Stock, *THIS JOURNAL*, **79**, 5175 (1957).

TABLE III
EVALUATION OF σ^+ CONSTANTS FROM *meta* AND *para* REACTIVITY DATA FOR THE BROMINATION OF SUBSTITUTED POLYMETHYLBENZENES

Aromatic compound	Substituent examined	Reference for (k/k_0)	σ^+ (This work)	σ^+ (Brown and Okamoto)	σ^b
Pentamethylbenzene (3-methylidurene)	<i>p</i> -CH ₃	4 ^a	-0.314	-0.306 ± 0.048	-0.170
3-Fluorodurene	<i>p</i> -F	2	-0.076	-0.071 ± 0.050	.062
3-Chlorodurene	<i>p</i> -Cl	2	.0965	.112 ± 0.047	.227
3-Bromodurene	<i>p</i> -Br	2	.139	.148 ± 0.043	.232
3-Iododurene	<i>p</i> -I	2	.126	.132 ± 0.044	.276
3-Cyanodurene	<i>p</i> -CN	Table I	.634	.659 ^c	.660
2-Cyanomesitylene	<i>m</i> -CN	Table I	.686 ^d	.562 ^e	0.56, 0.61, 0.68 ^e

^a See also ref. *b* in Table II. ^b All the values given below were taken from ref. 10 except when otherwise indicated. ^c Private communication from Professor H. C. Brown. ^d A value of 0.697 is obtained directly from the relative reactivity of cyanomesitylene. The value in the table is corrected on the basis of the mean factor of 1.5 discriminating between the mesitylene and isodurene series (see note *a*, Table II). ^e First value from the dissociation constant of benzoic acid (see note *c*). The second value is averaged from four different reactions (J. D. Roberts and W. T. Moreland, *THIS JOURNAL*, **75**, 2170 (1953) and refs. therein). The third value, which is the highest reported one, is from the reaction of phenoxide ions with ethylene and propylene oxides (see ref. 10).

σ^+ constants,³ as obtained from the solvolysis of substituted phenyldimethylcarbinyl chlorides, and with the side-chain σ constants.

Figure 1 and Table III indicate a number of interesting points. First of all, the effects of two halogens, fluorine and bromine, simultaneously attached to the mesitylene system appear to be strictly additive, thus lending further support to the validity of the polymethylbenzene approach even in regions of markedly low reactivity and with data obtained in the high concentration range used in this work.

Secondly, the σ_p^+ constants derived from the bromination of polymethylbenzenes agree closely with Brown and Okamoto's values well within the probable error established from a number of aromatic electrophilic reactions^{3b} and independently of the sign and magnitude of the component inductive and resonance effects of the *p*-substituents examined.¹⁵ Our σ_p^+ value for the cyano group (0.634) may be slightly too low; however, if allowance is made for the experimental reservations given in the results section, it is in even closer agreement with Brown and Okamoto's constant (0.659). We can consequently adopt Brown and Okamoto's σ^+ constants for all the *p*-substituents discussed in this paper.

In the third place, despite the validity of the assumption that the specific effects for the *m*-methyl group and the *m*-halogens are identical to those observed in side-chain reactions (σ_m^+ (aromatic bromination) = σ_m^+ (solvolysis of phenyldimethylcarbinyl chlorides) = σ_m), a relatively large discrepancy is observed between the σ_m^+ values for the *m*-cyano group in the two electrophilic reactions compared in Table III. In view of the reliability of the present reactivity data for cyanomesitylene (see Results section) and of the position of the substituent, *i.e.*, *meta* to the reacting center, it is difficult to offer an explanation for this discrepancy. Possibly, field and solvent effects play a role in deter-

(15) N. C. Deuo and W. L. Evans, *ibid.*, **79**, 5804 (1957), have recently computed σ^+ values for some halogens from aromatic chlorination data and found poor agreement with corresponding values from the solvolysis of phenyldimethylcarbinyl chlorides. This is clearly in contrast with the Fig. 2 reported in a previous paper³ and with the present results. Use of a reliable set of *meta* reactivity data would then appear to be essential in the investigation of the scope of equation 1.

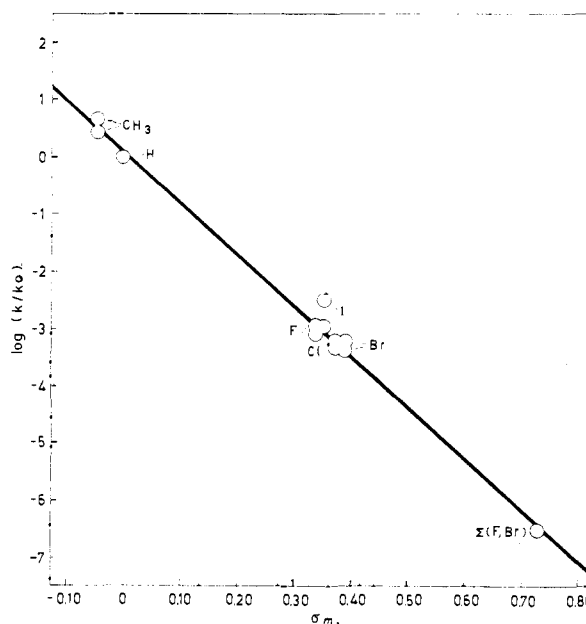


Fig. 1.— ρ - σ_m correlation for the bromination of polymethylbenzenes. For each substituent, the upper point refers to the isodurene series, the lower one to the mesitylene series; $\Sigma(F, Br)$ refers to fluorobromomesitylene.

mining it. It will be noted, at any rate, that for some reason the side-chain σ_m values themselves fluctuate over a similar range and that our σ_m^+ value is practically coincident to the highest existing σ_m value (0.68).

The relatively high σ_m^+ value obtained in this work for the cyano group corresponds to a relatively low reactivity: we have experienced a similar "over-all" phenomenon with the bromination rate of nitromesitylene (*m*-NO₂).¹ Professor H. C. Brown has drawn attention to this analogy by pointing out that since both *m*-cyano and *m*-nitro groups belong to the same electrical type, there may be a common factor in the polymethylbenzene approach, rather than in the nature of the reaction, leading to higher σ_m^+ values for these substituents. Unfortunately, the significance of the above analogy, though possibly real, is obscured by the different stereochemical requirements of the two groups, as may be shown

with the aid of Fisher-Hirschfelder molecular models. In the case of the bulkier nitro group any steric strain may be relieved partly through deviation from co-planarity, with no consequence on the rate of the reaction,¹ and partly through in-plane bond deflections of the adjacent methyl groups toward the seat of reaction, thus possibly reducing the reactivity (F-strain). Bond deflections of this kind have been postulated for nitromesitylene from dipole moment¹⁶ and infrared¹⁷ evidence. It would then appear that different factors also may be at work to account for the over-all effects of the two electrically similar groups.¹⁸

A final interesting point of the present data concerns the order of the σ^+ values for the *m* and *p*-cyano groups. The two values can be taken as essentially similar to each other with the peculiar trend $\sigma_m^+ > \sigma_p^+$. The same reactivity order indicated by this trend sometimes has been found in other, widely different reactions. For instance, it was observed in the reaction of the cyanobenzoic acids with diphenyldiazomethane in absolute ethanol¹⁹ and in the photochlorination of the cyanotoluenes.²⁰ Such cases would indicate a very small resonance contribution to the effect of the *p*-cyano group on reactivity.

Implications on the Orienting Effect of the Cyano Group.—Whatever the origin of the observed peculiarities may be, let us examine the implications of the reactivity data concerning the bromination of cyanopolymethylbenzenes on the orientation effects of the cyano group in a very similar reaction, *i. e.*, the bromination of benzonitrile. On considering the σ_m^+ and σ_p^+ values for this group nearly equal to each other with a trend $\sigma_m^+ > \sigma_p^+$, the present data would predict, for the bromination of benzonitrile with molecular bromine and under similar experimental conditions, a %*meta*/%*para* isomeric ratio approaching the statistical distribution, *i. e.*, 2:1, or even lower. This prediction is clearly in contrast with our common belief that the cyano group is predominantly *meta* orienting in bromination and would represent a serious breakdown of Holleman's rule for $-I(-T)$ substituents.²¹ This apparently odd prediction, however, deserves a few comments.

It must be pointed out that the halogenation of benzonitrile is, especially under conditions comparable to those of our measurements, a very difficult reaction; accordingly, the isomer distribution is not known. The only preparative study on this reaction, which reports on the isolation of *ortho* and *para* but not of *meta* derivatives,²² was carried out under conditions not suitable for discussion in this connection.

(16) A. C. Littlejohn and J. W. Smith, *J. Chem. Soc.*, 2476 (1957).

(17) A. Van Veen, P. E. Verkade and B. M. Wepster, *Rec. trav. chim.*, **76**, 801 (1957).

(18) Work is now in progress in this Laboratory to provide more conclusive evidence of F-strain effects caused by bond deflections in substituted polymethylbenzenes.

(19) J. D. Roberts, E. A. McElhill and R. Armstrong, *THIS JOURNAL*, **71**, 2923 (1949).

(20) C. Walling and B. Miller, *ibid.*, **79**, 4181 (1957).

(21) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Bell and Sons Ltd., London, 1953, p. 249. For the minor importance of the symbol $-T$ see p. 252.

(22) P. S. Varma and N. B. Sen-Gupta, *J. Indian Chem. Soc.*, **10**, 593 (1933).

Also, the cyano group is decidedly *meta* orienting in nitration.²³ A different behavior in bromination with Br_2 would find a theoretical support in the view²⁴ that a positively charged reagent, such as the nitronium ion, is responsible for a polarization of the ring *in the transition state*, which would be absent on the approach of a neutral reagent, such as the bromine molecule. In other words, the bromine molecule would not develop a sufficiently strong positive charge in the transition state to polarize the ring.

On the other hand, a differential behavior of a given substituent with respect to nitration with NO_2^+ and to bromination with Br_2 would be in contrast with a rigorous validity of the Hammett equation in the form 1 when applied to aromatic substitution. In the case of the methyl group such a validity is well illustrated by the excellent selectivity diagram discovered by Brown and his co-workers.²⁵ Nevertheless, in the case of other substituents, varying extents of dependence of the kinetic effects on mechanism might appear. A significant, though not very large, influence of this kind is clearly displayed by *p*-fluorine which acts as weakly activating (negative σ^+ value) in bromination²⁶ and as weakly deactivating (positive σ^+ value) in nitration.^{27,28} Such phenomena do not compromise the important role of the Hammett equation in the form 1, which can be soundly based on a convenient set of invariant σ_m constants; on the contrary, that equation may represent a solid basis to detect mechanism-dependent anomalies.²⁹

To sum up, it should be clear that the above considerations do not provide a proof for the orienting effect of the cyano group, but only illustrate the implications, right or wrong, on the problem from the polymethylbenzene approach and present some of the theoretical aspects involved. We are also pointing to the necessity of obtaining a direct proof by the halogenation of benzonitrile with molecular bromine. The scanty possibilities for the realization of such a proof now are being examined in this Laboratory.

Experimental

Materials.—The preparation and purification of the samples of 2-fluoro-4-bromomesitylene and 2-chloromesitylene used in the present rate measurements were described previously.^{2,30} 2-Cyanomesitylene and 3-cyanodurene were prepared in a straightforward manner according to the directions of Fuson, *et al.*,³¹ and purified by recrystallization from petroleum ether to constant melting point.

(23) J. W. Baker, K. E. Cooper and C. K. Ingold, *J. Chem. Soc.* 430 (1928).

(24) J. D. Roberts, R. A. Clement and J. J. Drysdale, *THIS JOURNAL*, **73**, 2181 (1951); B. M. Wepster, *Rec. trav. chim.*, **75**, 1473 (1956).

(25) H. C. Brown and C. R. Smoot, *THIS JOURNAL*, **78**, 6255 (1956); ref. 14; and H. C. Brown, J. D. Brady, M. Grayson and W. H. Bonner, *THIS JOURNAL*, **79**, 1897 (1957).

(26) P. B. D. de la Mare and P. W. Robertson, *J. Chem. Soc.*, 100 (1948); G. Illuminati and G. Marino, ref. 2; and this work, Table III.

(27) M. L. Bird and C. K. Ingold, *J. Chem. Soc.*, 918 (1938); N. C. Deno and R. Stein, *THIS JOURNAL*, **78**, 578 (1956).

(28) Examples of this effect also have been found by C. Eaburn, *et al.*, *J. Chem. Soc.*, 4858 (1956), and 4449 (1957), in other electrophilic aromatic substitutions.

(29) See also refs. 3b and 28.

(30) G. Grassini, G. Illuminati and G. Marino, *Gazz. chim. ital.*, **86**, 1138 (1956).

(31) R. C. Fuson and J. J. Denton, *THIS JOURNAL*, **63**, 654 (1941); R. C. Fuson, W. D. Emmons and J. P. Freeman, *ibid.*, **75**, 5322 (1953).

TABLE IV
TYPICAL KINETIC BROMINATION DATA IN NITROMETHANE
SOLUTION AT 30.0°^a

Time, min. × 10 ⁻²	Na ₂ S ₂ O ₄ , ml.	Blank corr. ^b	Corrected titer	Reacn., %
Fluorobromomesitylene				
0	8.61	0	8.61	0
10.32	8.25	0.025	8.275	3.89
15.80	8.10	.03	8.13	5.57
25.22	7.88	.04	7.92	8.01
30.50	7.79	.045	7.835	9.00
(33.75) ^c			(7.75) ^c	10
40.97	7.60	.055	7.655	11.09
Cyanomesitylene				
0	9.07			0
1.16	8.73			3.74
3.01	8.45			6.83
4.20	8.31			8.38
5.27	8.18			9.81
(6.00) ^c	(8.10) ^c			10
13.20	7.45			17.86
15.56	7.19			20.72
Cyanodurene				
0	8.92	0	8.92	0
10.90	8.79	0.02	8.81	1.23
25.10	8.68	.04	8.72	2.24
44.80	8.52	.07	8.59	3.70
68.60	8.40	.11	8.51	4.60
102.50	8.13	.15	8.28	7.18
125.50	7.98	.18	8.16	8.52
(150.90) ^c			(8.03) ^c	10

^a Kinetic solution (22 ml.) 0.055 *M* in both bromine and aromatic compound. Iodometric titrations with 0.025 *N* sodium thiosulfate on 2-ml. samples quenched in 5 ml. of a

4% KI solution in 70% ethanol. ^b Evaluated graphically in a separate blank experiment. ^c The values in parentheses are based upon graphic evaluation.

Nitromethane was purified according to the procedure described previously.² Kinetics blank experiments in this solvent showed that a slow consumption of bromine occurs in the order of about 1.6% in ten days, in the concentration range 0.03 to 0.06 *M*. These "bromine losses" are probably due to reaction with the solvent and not merely to volatility losses.

Kinetics Measurements.—The procedure used for the measurements was essentially the same as described previously except for the higher concentration of the two reactants. Allowance for the above-mentioned bromine losses was made in the case of fluorobromomesitylene and cyanodurene by running blank experiments with the same bromine concentration and evaluating the thiosulfate titer corrections graphically at any desired time. The reaction of cyanodurene was followed up to just less than 10% and the *t*₁₀ value was obtained by extrapolation. The usual interpolation procedure² was used instead for the evaluation of all the other data. Typical experiments and further details are reported in Table IV. The kinetics experiments were carried out in a dark room (red lamp).

All the results are summarized in Table I. The rates, *R*, relative to durene (= 1000) were calculated from the formula $R = 20.6 (t'_{10}/t_{10})$, where *t*'₁₀ and *t*₁₀ are the *t*₁₀ values for the substance of intermediate reactivity (chloromesitylene) and for that under examination, respectively, and 20.6 is the relative rate of chloromesitylene as reported previously.² The reactivities *k/k*₀ were obtained from the formula $k/k_0 = aR/R_0$, where *a* is the ratio of the statistical factor for the parent hydrocarbon over that for the substance under examination.

Acknowledgment.—The author is most grateful to Professor H. C. Brown for his helpful criticisms in reading the manuscript and for the numerous communications generously made available to him.

ROME, ITALY

[CONTRIBUTION FROM THE DEPARTMENT OF GENERAL CHEMISTRY OF THE UNIVERSITY OF ROME]

Relative Rates of Bromination of Some Hydroxy, Methoxy and Methylthio-substituted Polymethylbenzenes. Partial Inhibition of Resonance Effects¹

BY GABRIELLO ILLUMINATI

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The relative rates of bromination of hydroxymesitylene and of the methoxy and methylthio derivatives of mesitylene and durene have been measured in acetic acid solution at 30.0°. The methoxy and methylthio groups have been found strongly activating in the durene series and moderately deactivating in the mesitylene series. Steric inhibition of resonance in methoxydurene appears to be a relatively minor effect, even though it involves an increase in free energy of activation by about 2 kcal./mole. For the σ_m^+ constant of the hydroxy group a value of -0.133 has been calculated. The relation of the present data to *m* and *p* partial rate factors for the bromination of monosubstituted benzenes is discussed.

The free energy of activation for the resonance interaction of an electron-releasing substituent with the aromatic ring is an important stabilizing factor in the transition state of electrophilic reactions. Therefore, the phenomenon of steric inhibition of resonance resulting from deviation from coplanarity with the ring in such overcrowded compounds as substituted durenes should be best illustrated with non-symmetrical groups possessing a large electron-releasing capacity. The *p*-methoxy group seemed to be most suitable to such a study both because of experimental considerations

and of the availability of a sufficient amount of information about its effects on reactivity to permit a ρ - σ analysis. There seems to be only one preliminary report² on similar studies, one dealing with the effect of steric inhibition of resonance of the methoxy group on the aromatic bromination of 2-methoxy-*m*-xylene.

In this paper, the "polymethylbenzene approach" to orientation problems also has been extended to the *m*-hydroxy and *m*-methoxy substituents and to the next sub-group VIb analogs, the *m*- and *p*-methylthio substituents. Because of the expectedly minor importance of steric effects, con-

(1) This paper is part IX in the series "Substitution in Polymethylbenzenes"; Part VIII, G. Illuminati, *THIS JOURNAL*, **80**, 4941 (1958).

(2) Quoted, as unpublished work by F. A. Whittaker, by L. A. Wiles, *Chem. Revs.*, **56**, 329 (1956).