without a solvent. A very small yield (about 7%) of II was obtained by *several days'* heating of the dichloroquinone and trichlorophenol in benzene on the steam-bath but the time involved was so long that the result could have been due to oxidation by the air.

No way was found by which III could be formed either from I or II by the action of trichlorophenol.

Summary

1. The oxidation of *sym.*trichlorophenol yields not only 2,6-dichloroquinone as reported by previous investigators, but also a dinuclear product, 2-chloro-6-(2′,4′,6′-trichlorophenoxy)-*p*-benzoquinone, and a trinuclear product, 2,6-di-(2′,4′,6′-trichlorophenoxy)-*p*-benzoquinone.

2. The formation of these new products is interpreted as due to the intermediate formation of unsaturated radicals, of the general types $C_6H_2X_3O$- and —$C_6H_2Cl_2O$-.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

STUDIES ON THE DIRECTIVE INFLUENCE OF SUBSTITUENTS IN THE BENZENE RING. V. SOME SUGGESTED RELATIONS BETWEEN DIRECTIVE INFLUENCE AND THERMAL DATA[1]

BY A. W. FRANCIS, DONALD H. ANDREWS AND JOHN JOHNSTON

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The purpose of this paper is to point out some seeming parallelisms between the relative effect of the presence of a group in an aromatic compound upon its melting and boiling temperature and heat of melting, on the one hand, and the directive influence of the group, on the other. These parallelisms indicate that the directive influence is a permanent specific characteristic of the whole molecule rather than a temporary factor brought into play only at the moment of reaction through some "activation" process—an indication which is significant in connection with the mechanism of such reactions. In one sense this deduction is hardly novel, for it implies that the reactivity of certain classes of compounds is a function of structure just as melting temperature and heat of melting are; on the other hand, a connection between reactivity and structure would not at present be accepted as valid for all classes of compound and reaction, since it implies that catalysts would be without effect upon the relative order of the rates of reaction.

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[1] An elaboration of Part III of a dissertation presented by Alfred W. Francis in June, 1924, to the Graduate School of Yale University in candidacy for the degree of Doctor of Philosophy. It was presented in part at the sixty-ninth meeting of the American Chemical Society, Baltimore, April, 1925.

In a previous paper[2] we have presented estimated velocity constants of bromination of a series of derivatives of aniline and phenol, and have pointed out that these several velocities are in general accord with the idea that the directive influence of the groups already present makes itself evident as a relative acceleration of one or other of the possible reactions. These results are in good accord with the conclusions of Holleman,[3] who arranges the groups in order of the strength of directive influence as follows: for the *ortho-para* series, $OH > NH_2 > IBr > Cl > CH_3$, and for the *meta* series, $COOH > SO_3H > NO_2$. Several attempts have been made to relate directive influence to some chemical property of the group or of its compounds (for example, the rules of Crum Brown and Gibson[4] and of Vorländer).[5] J. J. Thomson[6] has suggested a possible connection between directive influence and dielectric capacity, and Rule and Patterson[7] have pointed out possible relations between dielectric capacity, optical activity and ionization constants of the substituted benzoic acids. The difficulty in making such comparisons arises from the lack of systematic reliable data on series of organic compounds; so we were led to examine melting and boiling temperatures, which are fairly complete, though the data in the literature are not all so accurate as is desirable.

In Table I are given the freezing and boiling temperatures and dielectric constants of the series of compounds[8] C_6H_5X and HX, the sequence of X being (except for CHO) that given by Holleman; and it is clear that there is a parallel progression. The heats of vaporization, in so far as they are available, show a similar regularity, as might be expected from the approxi-

TABLE I

PARALLELISM BETWEEN THE ORDER OF DIRECTIVE INFLUENCE OF A GROUP X AND THE FREEZING AND BOILING TEMPERATURES AND DIELECTRIC CONSTANT OF LIQUIDS CONTAINING X

	Favoring *o* – *p*						Favoring *m*			
X =	OH	NH_2	Br	Cl	CH_3	H	CHO	NO_2	SO_3H	COOH
C_6H_5X										
Freezing temp.	42	−6	−31	−45	−94	5	−13	5	66	121
Boiling temp.	183	184	156	132	110	80	179	210	..	249
Dielect. const.	9.7	7.3	5.2	11	2.3	2.3	18	36	..	...
HX										
Freezing temp.	0	−77	−87	−112	−184	−259	..	...	..	9
Boiling temp.	100	−39	−69	− 83	−153	−258	−21	...	..	101

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[2] Francis, Hill and Johnston, THIS JOURNAL, **47**, 2211 (1925).

[3] Holleman, *Chem. Reviews*, 1, 202 (1924).

[4] Crum Brown and Gibson, *J. Chem. Soc.*, **61**, 367 (1892).

[5] Vorländer, *Ann.*, **320**, 122 (1902).

[6] J. J. Thomson, *Phil. Mag.*, **46**, 497 (1923).

[7] Rule and Patterson, *J. Chem. Soc.*, **125**, 2155 (1924).

[8] As taken from Landolt-Börnstein "Tabellen," 5th ed., Julius Springer, Berlin, 1923; the temperatures are here given only to the nearest degree.

mate validity of Trouton's rule; the heats of melting—for which there is no corresponding rule—will be discussed later.

Table II is a similar arrangement of the melting temperatures of three series of the three isomeric disubstituted benzene derivatives C_6H_4XY; and the same regularity is apparent, there being only a few exceptions. Data for four other series—namely for X = NH_2, Br, CH_3 and NO_2—are also available, and show the same type of sequence. The boiling temperatures show a precisely similar regularity, and so are omitted for the sake of brevity; in this connection it is worth noting that the boiling temperatures lie within a smaller temperature range, and that those of the three isomers of a given composition usually differ by less than 10°, as contrasted with frequent differences of more than 100° in the corresponding freezing temperatures. This has been pointed out by Sidgwick and Callow,[9] who state that the vapor pressure and solubility relations in the liquid state are "in the majority of benzene derivatives very little influenced by the orientation of the substituents" but that "the solubility of the solids is largely determined by the crystalline forces, which themselves are greatly affected by the orientation."

TABLE II

VARIATION OF MELTING TEMPERATURE OF C_6H_4XY WITH DIRECTIVE INFLUENCE OF THE SUBSTITUENTS

X		Y = OH	NH_2	Br	Cl	CH_3	CHO	NO_2	SO_3H	COOH
OH	*o*	105	176	6	7	30	−7	45	...	155
	m	112	123	32	28	4	108	96	...	188
	p	172	184	64	37	37	115	113	...	210
Cl	*o*	7	0	−13	−17	−34	110	33	...	137
	m	28	−10	−21	−24	−48	17	45	...	153
	p	37	70	65	53	7	48	84	...	236
COOH	*o*	155	145	150	137	104	97	147	250	203
	m	188	180	155	153	111	165	141	141	300
	p	260	187	251	236	179	246	238	259	...

This table brings out another point which serves to distinguish between the two types of groups. The melting temperature of the *para* isomer in most of the simpler types of compounds is the highest of the three, whereas the lowest may be either the *ortho* or the *meta*, with equal probability. Now it appears that if both groups X and Y are *like* in directive influence, the freezing temperature of the *meta* compound is usually lowest; whereas, if X and Y are *unlike*, that of the *ortho* is usually lowest. These observations can be coördinated if we consider that in the former case the directive influences of the two substituents coöperate in the *meta* isomer, but oppose one another in the *ortho* and *para;* whereas, when the groups are unlike, there is coöperation in the *ortho* and *para* isomers but opposition in the *meta*. Thus, it appears that as between *ortho* and *meta* isomers, that one which is

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[9] Sidgwick and Callow, *J. Chem. Soc.*, **125**, 529 (1924).

the more reactive has usually the lower melting temperature. This will be clearer from Table III in which we include all of the commoner systems for which the melting temperature of both *ortho* and *meta* is known, the criterion of commonness being that both isomers are mentioned in a recent catalog of organic chemicals;[10] of the 30 pairs, 25 follow the rule stated above.

TABLE III

COMPARISON OF MELTING TEMPERATURES OF COMMON ORTHO AND META ISOMERS

Like controlling groups			Unlike controlling groups		
	Ortho	*Meta*		*Ortho*	*Meta*
Aceto-aminophenols	203	148	Aceto-aminobenzoic acids	185	250
Aminophenols	174	122	Aminobenzoic acids	145	180
Bromo-anilines	31	18	Bromobenzoic acids	150	155
Bromotoluenes	−26	−40	Chlorobenzoic acids	142	158
Chloro-anilines	0	−10	Hydroxybenzoic acids	158	200
Cresols	30	11	Methyl nitrocinnamates	73	124
Dichlorobenzenes	−18	−25	Nitro-anilines	73	116
Dinitrobenzenes	118	90	Nitro-anisoles	9	35
Nitrobenzoic acids	148	141	Nitrophenols	45	97
Phenylenediamines	103	63	Nitrotoluenes	−10	16
Toluidines	−21	−31[a]	Nitro-chlorobenzenes	32	45
Xylenes	−27	−54	Nitro-bromobenzenes	43	56
Xylyl bromides	95	77			
			Nitro-iodobenzenes	49	35
			Nitrocinnamic acids	245	200
Chlorophenols	9	33			
Ethyl nitrobenzoates	30	47			
Methyl nitrobenzoates	13	78			

[a] This temperature is not given in the literature. It was determined experimentally by a time-temperature cooling curve upon a sample of *m*-toluidine especially purified by fractional distillation and fractional crystallization.

When the test of the rule is extended to all of the 357 systems for which the necessary data are to be found in Richter's "Lexikon" or in Beilstein's "Handbuch," the list of groups concerned includes a large number of complex radicals whose directive influence is less pronounced, and less well established, than that of the simpler groups already considered; and consequently the basis of comparison is less certain. But we present a summary of the results derived on the basis (1) that the category of *meta*-controlling groups includes all derivatives of quinquivalent nitrogen, hexavalent sulfur, —CO—, —CN, —CCl_3, (2) that the *ortho-para* category includes all derivatives of trivalent nitrogen, bivalent sulfur, the halogens, —O—, —CH— (except —CHO and —CHN—), —C_6H_5 and its derivatives. This summary shows that the rule holds in about two-thirds of all the cases, as compared with five-sixths of the cases in which we are surer as to the directive influence to be ascribed to the groups. Inciden-

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[10] Eastman Kodak Co., Catalog No. 14.

tally it may be mentioned that the so-called "normal" order (*o*, *m*, *p*) of melting temperatures is found in just one-half of these cases, thus showing the lack of such a "normal" order.

TABLE IV

SUMMARY OF CASES TESTED FOR RULE OF MELTING TEMPERATURES

Group	Number of cases		Aggregate temp. Differences	
	Rule holds	Rule fails	Rule holds	Rule fails
NO_2	47	29	1401	850
CH_3	47	17	1660	475
OH	29	14	1108	469
NH_2	17	5	663	113
Cl	19	11	441	230
Br	14	9	333	124
I	12	7	264	112
COOH	21	14	795	523
$NHCOCH_3$	11	5	444	127
Two substituents identical	25	13	741	383
Miscellaneous	15	16	389	328
Total	257	140	8239	3734
Cases counted twice	32	8	800	188
Net total	225	132	7439	3546

Quite recently Pastak[11] has published two papers dealing with the melting temperatures of series of benzene derivatives, the first treating isomers with identical substituents, the second those with different substituents; and his conclusion is essentially the same as that just discussed and illustrated in Tables III and IV. Thus Pastak writes: "The normal position of the radicals is *meta* (non-quinogen) when both belong to the same series,[12] but, when each belongs to a different series, the normal position is *ortho* and *para* (the quinogen positions). . . .On the basis of this classification, one may formulate the principal rule with reference to their melting temperatures: The normal[13] isomer (hence, the more stable) has the lower melting temperature." He also, with the aid of certain geometrical postulates, extends his rule to tri-, tetra-, penta- and hexa derivatives, containing not more than two different substituent groups, and finds satisfactory regularity.

The fact that, of the three isomers, the *para* has the highest melting temperature has by some been interpreted as a consequence of its being the most "symmetrical." May one, on this basis, argue that the *ortho* or the *meta*, according as one or other melts lowest, is the least symmetrical? and if so, may one combine this idea with the rule discussed above and hazard the statement that, of the two isomers, that which reacts more read-

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[11] Pastak, *J. Chim. phys.*, **22**, 48, 264 (1925).

[12] His series are: (1) (basic) CH_3, Cl, Br, OH, NH_2; (2) (acidic) COOH, NO_2.

[13] The "normal" isomer is in the first case the *meta*, in the second the *ortho*.

ily (as a liquid) is the less symmetrical, thus relating the directive effect of the groups to the degree of symmetry of the compound? The main difficulty in making a test of this speculation would lie in assigning a degree of "symmetry," which might be chosen either as a geometrical concept (if the crystallographic data were available) or, perhaps preferably, as equivalent to degree of polarity[14] and associated, therefore, with the lack of uniformity of the electric field about the molecule. This is suggested by the fact that the melting temperature of a typical non-polar compound, such as methane, is lower than that of similar polar compounds such as ammonia or water. On the other hand, we must recognize that melting temperature is not a function of the crystal structure alone, but depends also upon the constitution of the liquid in contact with the crystals, although, in the case of pure liquids, the constitution is again determined by the molecular forces.

There is another apparent parallelism, which for lack of data can be

TABLE V

ENTROPY OF MELTING OF SERIES OF ORTHO, META, PARA ISOMERS

Substituents	Heat of melting Kilocal./mole			Melting temp. °T (abs.)			Entropy of melting cal./mole/degree		
	o	p	m	o	p	m	o	p	m
	Substituents of unlike directive influence								
COOH, CH_3[a]	4.8	5.4	3.8	377	453	382	12.8	12.0	9.8
COOH, NH_2[a]	4.7	5.0	5.2	418	462	453	11.3	10.8	11.5
COOH, Cl[a]	6.2	7.7	5.7	413	513	427	14.9	15.0	13.3
NO_2, NH_2[a]	3.9	5.0	5.7	342	421	385	11.2	12.0	14.7
NO_2, Cl[b]	3.9	3.6	5.2	306	356	317	12.7	10.1	16.4
NO_2, Br[c]	4.2	5.5	4.9	314	398	329	13.4	13.8	14.9
NO_2, CH_3[c]	2.8	3.8	3.3	269	327	289	10.4	11.5	11.5
	Substituents of like directive influence								
NO_2, NO_2[a]	5.5	6.7	4.2	390	447	363	14.0	15.0	11.4
NO_2, COOH[a]	6.7	8.8	4.6	419	512	414	16.0	17.2	11.1
OH, OH[a]	5.4	6.5	5.1	377	445	383	14.4	14.5	13.3
OH, Cl[c]	2.6	2.9	2.8	280	310	302	9.4	9.3	9.3
Cl, Cl[d]	3.1	4.3	3.0	256	326	249	12.1	13.3	12.1
Br, Br[d]	3.0	4.9	3.2	275	360	266	11.0	13.6	11.9
I, I[d]	3.4	5.3	3.8	297	402	307	11.3	13.3	12.4
Cl, Br[d]	3.0	4.5	2.9	261	338	252	11.3	13.3	11.6
Br, I[d]	3.5	4.7	2.9	275	363	264	12.5	12.9	11.0
CH_2Cl, CH_2Cl[e]	5.1	5.7	4.7	328	373	307	15.5	15.3	15.2
CH_2Br, CH_2Br[e]	6.4	...	5.6	368	...	350	17.4	..	16.0

[a] Calorimetric determinations; Andrews, Lynn and Johnston, Ref. 15.

[b] Kohman, *J. Phys. Chem.*, **29**, 1048 (1925); from mutual solubility.

[c] Jona, *Gazz. chim. ital.*, **39**B, 289 (1909); from solubility.

[d] Narbutt, *Z. Elektrochem.*, **25**, 51 (1919); calorimetric.

[e] Colson, *Compt. rend.*, **104**, 429 (1887); calorimetric.

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[14] In the sense used by Bray and Branch [THIS JOURNAL, **35**, 1440 (1913)] and by Lewis [*ibid.*, **35**, 1448 (1913)]. There is as yet, however, no direct measure of polarity.

tested in only a few cases, between entropy of melting of the isomers, C_6H_4XY, and the similarity of directive influence of X and Y. In Table V, we have assembled the values of entropy of fusion of the three isomers, C_6H_4XY, in all cases for which we were able to find the heats of melting. The majority of these are calorimetric determinations, some of which, however, may possibly be in error by several hundred calories;[15] the others were derived from the mutual solubility curves,[16] and may be subject to an uncertainty of the *same* magnitude.[17] This table shows that, if the two substituent groups are of unlike directive influence, the entropy of melting of the *meta* (the slowest to react) is higher than that of the *para* in five cases out of the seven; whereas with like groups, the *meta* (which in these cases normally reacts faster than either of the others) has in all the cases a smaller entropy of melting than the *para*. The comparison between *meta* and *ortho* is less clear cut, but there are indications of analogous conclusions.

We were led to look into this question by the following considerations which, it is admitted, do not constitute a rigorous train of reasoning. According to the so-called third law of thermodynamics, the entropy of a pure crystalline substance is zero at the absolute zero; consequently, the entropy at ordinary temperature of two crystalline substances, each stable throughout the temperature range, will be the same, provided that the two heat-capacity curves are identical. This condition appears to be substantially fulfilled[18] in the case of *ortho*, *meta* and *para* isomers; and so we assume that the entropy of all three solids is the same at 25°, and, as a direct corollary, that the differences in entropy as between the three substances *as liquids* would be substantially the differences in entropy of fusion. On this basis, when each isomer separately undergoes some reaction, for example, is brominated, the tendency to react (as measured by the change in free energy) would be greatest in the case of the isomer with the smallest entropy of fusion, provided that the entropy of the products be equal—a rather daring assumption with respect to which there is at the moment no evidence available. Now it was of interest to ascertain if there be any parallelism between the relative tendency of three liquid isomers to react (as inferred from the relative values of the entropy of melting) and the relative rate of the three similar reactions, some measurements of which have recently been published.[3] In general, there has proved to be absolutely no correlation of free-energy changes and rate of a reaction; but

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[15] See Andrews, Lynn and Johnston, THIS JOURNAL, **48**, 1274 (1926).

[16] From the initial slope of the graph of log N_A versus $1/T$, N_A being the mole fraction of A in the solution at the absolute temperature T.

[17] Indeed the disparity may be thousands of calories if derived from the solubility in an ordinary solvent; for example, for *p*-dihydroxybenzene, Mortimer [THIS JOURNAL, **44**, 1428 (1922)] gives 3220, the observed being 6200 cal.

[18] See Andrews, THIS JOURNAL, **48**, 1287 (1926).

we were emboldened to think that, nevertheless, there might be some parallelism in the very restricted type of case under discussion, particularly as the experiments showed that the *relative* rate was practically independent of concentration or temperature within a reasonable range of variation of conditions. The fact that the expectation based upon these assumptions is largely fulfilled is no proof of the validity of the assumptions, but it suggests further inquiries and we give it here in the belief that any indication may be valuable in a field in which so little is known definitely.

Summary

We have pointed out some seeming parallelisms between the melting temperature of a benzene derivative and the character of the radical, or radicals, present, particularly with respect to whether the directive influences assigned to these radicals are like or unlike. For example, when they are like, the *meta* isomer usually has the lower melting temperature; when unlike, the *ortho* melts lower.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 4]

STUDIES ON THE DIRECTIVE INFLUENCE OF SUBSTITUENTS IN THE BENZENE RING. VI

BY A. W. FRANCIS[1]

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In Part II[2] a method was described by which the relative rates of bromination of various aromatic amino and phenolic compounds were measured in aqueous solution. From the results attempts were made to estimate the directive influence of the substituents in these compounds. The present paper is a continuation of that investigation, applying the method to a much larger number of compounds and discussing the results more fully than was possible at that time.

In brief, the method consists in making competition experiments by adding to a mixture of two compounds an insufficient amount of a reagent which reacts with both, and by suitable analysis determining the extent of each reaction. When two organic compounds were competitors, the reagent was a standard bromide-bromate solution, which with acid generates bromine, and the analysis consisted usually in estimating gravimetrically the highest brominated product of one of the competitors. There was also a considerable number of competitions between organic compounds and inorganic reducing agents, which are oxidized by bromine. In these the reagent was free bromine water,[3] and the analysis was

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[1] National Research Fellow in Chemistry.

[2] Francis, Hill and Johnston, THIS JOURNAL, **47**, 2211 (1925).

[3] Francis, *ibid.*, **48**, 655 (1926).