159. *The Kinetics of Anionotropic Rearrangement. Part IX. The Effects of Polycyclic Aromatic Substituents on Reactivity. A Comparison of the Electronic Properties of the Phenyl, 1-Naphthyl, 2-Naphthyl, 9-Anthryl, and 9-Phenanthryl Groups.*

By E. A. Braude and J. S. Fawcett.

The kinetics of the acid-catalysed oxotropic rearrangements of a number of polycyclic 1-aryl-3-methylallyl alcohols (I) to the corresponding 3-aryl-1-methylallyl alcohols (II) have been determined in aqueous dioxan solution. The results are compared with those previously obtained for the rearrangement of 1-phenyl-3-methylallyl alcohol (phenylpropenylcarbinol) (I; X = Ph) and appear to provide the first comprehensive set of quantitative kinetic data on a series of polycyclic aromatic derivatives. The rate constants at one temperature increase in the sequence 9-phenanthryl < phenyl < 2-naphthyl ~ 1-naphthyl < 9-anthryl, but the differences are relatively small and there is little variation in either the energies of activation or the probability factors.

The results are discussed in relation to existing evidence concerning the reactivity of polycyclic aromatic systems. Qualitatively, they are in agreement with the predictions of both valency-bond resonance and molecular-orbital theory, except for the phenanthryl derivative. An explanation for this anomaly is suggested. Quantitatively, the results for the naphthyl and anthryl derivatives show a closer correlation with simple valency-bond resonance theory than with molecular-orbital calculations, and a linear relation is found to hold between the rate constants at one temperature and the expected number of contributing polar resonance forms.

In earlier work in this series (Part V, *J.*, 1946, 396; Part VI, *J.*, 1947, 1096; Part VIII, *J.*, 1948, 1982), the rearrangement of 1-phenyl-3-methylallyl alcohol (phenylpropenylcarbinol) (I; X = Ph) to 3-phenyl-1-methylallyl alcohol (styrylmethylcarbinol) (II; X = Ph) has been investigated in some detail. The isomerisation proceeds with great facility and without side reactions in dilute acid solution, and its mechanism under these conditions can now be regarded as established with a reasonable degree of certainty. It has also been shown that this type of rearrangement is very sensitive to structural changes, being facilitated by electron-donating and hindered by electron-attracting substituents, as required by its mechanism. Since a wide variety of analogues of 1-phenyl-3-methylallyl alcohol is fairly readily accessible synthetically, this affords an excellent basis for investigating the electronic properties of substituents which have not yet been studied in this respect because of a lack of suitable reactions or for other reasons. This applies to a surprisingly large number of common and important groups. Polycyclic and heterocyclic organic chemistry, in particular, are almost devoid of quantitative reactivity data, and theoretical work has considerably outstripped experimental advances in this field.

$$\text{(I.)}\quad X\cdot CH(OH)\cdot CH{:}CHMe \longrightarrow X\cdot CH{:}CH\cdot CH(OH)\cdot Me\quad \text{(II.)}$$

The present communication deals with a kinetic study of the rearrangements of some polycyclic 1-aryl-3-methylallyl alcohols (I; X = 1-naphthyl, 2-naphthyl, 9-anthryl, and 9-phenanthryl), the synthesis and rearrangements of which have been described (Braude, Fawcett, and Newman, preceding paper). The rate constants, energies of activation, and probability factors under standard conditions employed in earlier studies are collected in Tables I and II. As before, the reaction rates were determined spectrometrically, advantage being taken of the differences between the ultra-violet light absorption of 1-aryl-3-methylallyl and the isomeric 3-aryl-1-methylallyl alcohols. A complication arose with the 9-anthryl derivative owing to the intense fluorescence of the rearranged carbinol, but this could be overcome by suitable choice of wave-lengths (see Experimental). Good first-order rate constants were obtained throughout, and the final absorption intensities at the wave-lengths chosen were identical within experimental error with those of the pure 3-aryl-1-methylallyl alcohols, showing that no measurable equilibria were set up. The usual solvent effects were observed, the rate constants being decreased about threefold, and the Arrhenius energies of activation increased by about 3 kcals./mol., in 80% as compared with 60% aqueous dioxan. The rate constants at one temperature increase in the sequence 9-phenanthryl < phenyl < 2-naphthyl ≈ 1-naphthyl < 9-anthryl, but the differences are small and only cover a range of fivefold variation. The values for the two naphthyl derivatives lie especially close together and their order depends on the temperature, the rearrangement of the 1-naphthyl derivative being a little faster below 50°, and a little slower above 50°, than that of the 2-naphthyl derivative. The Arrhenius energies of activation and probability factors for a particular medium are practically constant throughout the series; the differences in energy of activation only slightly exceed the uncertainty in the Arrhenius plots (*ca.* $\pm 0{\cdot}3$ kcal./mol.).

The rearrangement of the lower homologues, 1-naphthyl- and 2-naphthyl-vinylcarbinol, has been examined qualitatively by Burton (*J.*, 1931, 759), who concluded from indirect evidence (the degree of rearrangement accompanying *p*-nitrobenzoylation) that the ease of isomerisation increases in the order phenyl < 2-naphthyl < 1-naphthyl.

TABLE I.

First-order rate constant (10^4 k, *min*$^{-1}$.) *for the rearrangements of* 1-*aryl*-3-*methylallyl alcohols* (I) *to* 3-*aryl*-1-*methylallyl alcohols* (II) *in aqueous dioxan*–0·01M-*hydrochloric acid.*

[Concentration of alcohols, 0·001—0·01M.; c_S = dioxan concentration (% v/v).]

Temp.	c_s.*	X = Phenyl.[1]	2-Naphthyl.	1-Naphthyl.	9-Anthyrl.	9-Phenanthryl.
0°	60	5·4	8·0	8·3	25	4·0
30	60	184	320	345	805	146
	80	69	126	129	315	66
40	60	545	800	840	2,050	445
	80	—	400	405	1,050	210
50	60	1510	2450	2450	6,500	1280
	80	—	1300	1180	3,200	700
60	60	3650	6100	5300	14,500	3200
	80	—	3300	2900	6,650	1890

* Values for c_s = 80% at 0° are omitted, as solid dioxan tended to crystallise in the media.

[1] Braude, Jones, and Stern, *J.*, 1946, 396. The value for c_s = 80% at 30° is extrapolated from measurements at higher acid concentrations.

TABLE II.

Relative rate constants (r), *Arrhenius energies of activation, and probability factors.*

($k/c_A = Ae^{-E_{Arr.}/RT}$, where c_A = acid concentration.)

	60% Aqueous dioxan.			80% Aqueous dioxan.		
X.	*r.**	$E_{Arr.}$.	log *A*.	*r.**	$E_{Arr.}$.	log *A*.
Phenyl[1]	1	19·5	12·6	1	—	—
2-Naphthyl	1·74	20·2	13·3	1·82	22·4	14·5
1-Naphthyl	1·88	19·9	13·1	1·87	22·0	14·2
9-Anthryl	4·37	19·5	13·2	6·32	22·0	14·6
9-Phenanthryl	0·80	20·3	13·1	0·96	22·6	14·4
(Vinyl[2])	0·78	—	—	0·67	—	—

* At 30°.

[1] Braude, Jones, and Stern, *loc. cit.*

[2] Braude and Jones, *J.*, 1946, 128. (Extrapolated from measurements in aqueous ethanol.)

DISCUSSION.

(1) *Correlation of Available Data on the Reactivity of Polycyclic Aromatic Compounds.*—The reactivity of the polycyclic aromatic hydrocarbons is generally stated to increase in the order benzene < naphthalene < phenanthrene < anthracene. This sequence is based on a wealth of *qualitative* data concerning, particularly, the ease of sulphonation, nitration, bromination, hydrogenation, and oxidation, and although it is a commonplace that such qualitative comparisons of reactivity without kinetic control can be misleading, there is no reason to doubt the validity of the general result in the present case. The reactions enumerated above include both heterolytic and homolytic types, and it is of some interest that the different types of reactivity appear to run parallel in this series; however, we are here concerned only with heterolytic reactivity and therefore confine attention to sulphonation and nitration which almost certainly involve attack by the entities SO_3H^+ and NO_2^+ under the usual conditions (for references, see Braude, *Ann. Reports*, 1949, **46**, in the press). The results for naphthalene are clear-cut, both sulphonation and nitration proceeding with comparable speed at lower temperatures than those required for benzene, and substitution in the 1- being somewhat faster than in the 2-position. Phenanthrene is sulphonated and nitrated with comparable speed at a lower temperature than naphthalene, but the evidence concerning the reactivity of the different positions is somewhat conflicting; it appears that the 9-, 2-, and 3-positions are most readily substituted, with the reactivity probably decreasing in that order (cf. Fieser, *J. Amer. Chem. Soc.*, 1929, **51**, 2460). Finally, anthracene undergoes electrophilic substitution somewhat more readily still, but here sulphonation is faster in the 1- and 2-positions, whereas nitration is fastest in the 9-position. The abnormal orientation of the sulphonation of anthracene is probably due

to steric hindrance which will first become effective at the " flanked " *meso*-positions and with large reagents, such as SO_3H^+.

Some kinetic measurements on the halogenation of polycyclic aromatic hydrocarbons have been recorded (Lauer and Oda, *Ber.*, 1936, **69**, 141, 146, 851; Robertson, De La Mare, and Johnston, *J.*, 1943, 276; De la Mare and Robertson, *ibid.*, p. 279; Wibaut and Sixma, *Proc. K. Akad. Wetensch. Amsterdam*, 1948, **51**, 776), but they do not readily lend themselves to comparison owing to the different conditions employed and owing to the incursion of catalytic effects; the brominations of anthracene and phenanthrene are further complicated by the simultaneous occurrence of substitution and addition reactions (Price, *J. Amer. Chem. Soc.*, 1936, **58**, 1834, 2101; Fieser and Price, *ibid.*, p. 1838).

Most of the scant *quantitative* data to be found in the literature regarding the reactivity of polycyclic aromatic compounds, as well as the present results, concern side-chain reactions (see Table III). Shoesmith and Rubli (*J.*, 1927, 3098) and Ingold and Patel (*J. Indian. Chem. Soc.*, 1930, **7**, 95) investigated the neutral hydrolysis and alcoholysis of benzyl, 2-naphthylmethyl, and 1-naphthylmethyl bromides in 90% aqueous alcohol and obtained rate constants increasing in that order. Bergmann and Hirshberg (*J.*, 1936, 331) determined the rates of alkaline hydrolysis of methyl 1- and methyl 2-naphthoate in aqueous methanol of unstated composition and found that the 1- reacted slightly faster than the 2-naphthyl ester. The rate constants for both naphthyl derivatives are smaller than a quoted value for methyl benzoate, but this comparison may not be significant since the solvent conditions are not necessarily identical. Recently, Gordon, Miller, and Day (*J. Amer. Chem. Soc.*, 1948, **70**, 1946; 1949, **71**, 1245) have measured the rates of ammonolysis of alkyl and aryl acetates in anhydrous ethylene glycol and found that the naphthyl esters react about 100 times more *slowly* than phenyl acetate. The effective reagent in this reaction is believed to be a relatively large ammonia–glycol complex, and the exceptionally low reactivity of the polycyclic derivatives is ascribed to steric hindrance. The only previous kinetic data for polycyclic systems other than naphthyl derivatives appear to come from Shoppee's study (*J.*, 1933, 40) of the reversible prototropic rearrangements of 1-phenyl-3-arylmethyleneazomethines. The order of mobilities was found to be 9-phenanthryl $<$ 2-naphthyl $<$ 1-naphthyl, but no value could be obtained for the phenyl substituent since the 1 : 3-diphenyl derivative is completely symmetrical.

TABLE III.

Relative reactivities (reaction rates) of polycyclic aromatic derivatives.

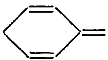
X.	(1).	(2).	(3).	(4).	(5).	(6).
Phenyl	[1]	1	—	1	—	1
2-Naphthyl	[2]	1·74	0·88	1·68	0·83	0·01
1-Naphthyl	[3]	1·88	1	2·16	1	0·01
9-Anthryl	[5]	4·37	—	—	—	—
9-Phenanthryl	[4]	0·80	0·65	—	—	—
(Vinyl)	—	0·78	—	—	—	0·24

(1) Sequence of ease of nitration of hydrocarbons derived from qualitative data. (2) Oxotropic rearrangement of 1-aryl-3-methylallyl alcohols at 30° (this paper). (3) Prototropic rearrangement of 1-phenyl-3-arylmethyleneazomethines at 86° (Shoppee, *loc. cit.*). (4) Neutral hydrolysis of arylmethyl bromides at 25° (Shoesmith and Rubli, *loc. cit.*). (5) Alkaline hydrolysis of methyl naphthoates at 60° (Bergmann and Hirshberg, *loc. cit.*). (6) Ammonolysis of aryl acetates at 30° (Gordon, Miller, and Day, *loc. cit.*).

Summarising the available evidence, and neglecting exceptions probably conditioned by steric hindrance, we find the same order of increasing heterolytic reactivity, phenyl $<$ 2-naphthyl $<$ 1-naphthyl $<$ 9-anthryl, to apply to both nuclear and side-chain reactions. The position of the 9-phenanthryl group, on the other hand, varies; it is below 9-anthryl in nuclear cationoid substitution, below naphthyl (and possibly phenyl) in side-chain prototropy, and below phenyl in side-chain oxotropy.

(2) *Qualitative Theory.*—The generally accepted basis of the electronic theory of substituent effects is that substituents increase or decrease, as the case may be, the electron-availability at the point of reaction and thereby increase or decrease the energy of activation (E) of the heterolytic fission, depending on the electronic requirements of the latter (cf. Hinshelwood, Laidler, and Timm, *J.*, 1938, 848). Steric and related factors, on the other hand, are known to influence both the energy of activation and the probability factor (A) or entropy of activation. The only comparable kinetic measurements on a series of polycyclic aromatic compounds which allow analysis of differences in activation energies and probability factors appear to be those reported in the present work. The total variation in rate constants is too small, however, to

provide a clear distinction as to the extent to which differences in E or A (both of which are almost within experimental uncertainty) contribute to variations in k. Nevertheless, since earlier work on the effects of benzenoid and other substituents (cf. Part VI, *J.*, 1947, 1096) and unpublished work on the effects of heterocyclic substituents has shown that differences in k were mainly due to differences in E, it will be assumed that the same applies in the polycyclic series. This assumption is supported by the work of Wibaut and Sixma (*loc. cit.*), according to which the differences in the rates of bromination of naphthalene in the 1- and the 2-position are almost entirely due to differences in E. It therefore appears justified, in the subsequent discussion, to employ differences in reaction rates directly as a measure of the electronic effects of substituents.

As previously (cf. Part VI, *loc. cit.*), we adopt Ingold's convention (*Chem. Reviews*, 1934, **15**, 233) of inductive (I) and tautomeric (T) effects, negative signs referring to electron-attraction and positive signs to electron-donation. The tautomeric effect falls into two parts, the permanent mesomeric (M) effect present in the ground state, and the additional electronic (E) effect, which represents a time-variable polarisability contribution operative in reacting molecules and reaches its maximum in the transition state. The time-variable counterpart of the inductive effect, the inductomeric effect, is likely to be small and is neglected. On this basis, the effect of a phenyl substituent is described as $-I,\pm T$. The $-I$ effect arises from the fact that the constituent atoms of a phenyl substituent, like those of any covalently unsaturated group, have less than their normal share of bonding electrons (the double-bond or π-electrons being less " bonding " than the single-bond or σ-electrons). The $-I$ effect would be expected to increase with increasing unsaturation in the sequence vinyl < phenyl < naphthyl < anthryl, phenanthryl, but to be much less than proportional to the number of double bonds in the substituent, since the additional unsaturation will be further and further removed from one particular point, and since the I effect, being mainly electrostatic in origin, rapidly decreases in the distance. The $\pm T$ effect of a phenyl substituent arises from the fact that it can partake of resonance forms of the type $+$$=X^-$ or of the type $-$$=X^+$ and that the polarity will be mainly determined by X. Since the number of possible polar forms increases in the sequence phenyl < 2-naphthyl < 1-naphthyl < 9-phenanthryl < 9-anthryl, the $\pm T$ effects would be expected to increase in that order. The actual reactivity sequence will depend on a combination of the I and T effects. In a reaction facilitated by electron-recession, the $-I$ and $-T$ effects will reinforce each other and the expected reactivity sequence is the same as for the T effects. In a reaction requiring electron-accession on the other hand, the $-I$ and $+T$ effects will oppose each other and the actual sequence will depend on the relative magnitudes of the two effects. These may vary from case to case, as with other $-I,+T$ substituents, such as the halogens. Whatever the resultant sequence, the reactivity differences will be smaller than with a reaction requiring electron-recession.

An estimate of the I effects alone may be derived from the dissociation constants of the arylcarboxylic acids, arylamines, and aryl-hydroxy-derivatives, if it is assumed that the $+T$ and $-T$ effects brought into play by the forward and backward reactions are of equal magnitude, so that the equilibria will be determined only by the $-I$ effects. (Detailed consideration shows that this assumption is likely to be only approximately correct.) The available data (Table IV) bear out the expected sequence of $-I$ effects, vinyl < phenyl < 2-naphthyl < 1-napthtyl < phenanthryl < anthryl. (In assessing the differences quantitatively, it must be remembered that the $-I$ effects will exert opposite effects on the rates of the forward and backward reactions, and that the effect will be magnified in the dissociation constant, which is the ratio of the two.)

TABLE IV.

Dissociation constants of aryl derivatives.

X.	$X{\cdot}CO_2H$ (in water) ($\times 10^5$).	$X{\cdot}CO_2H$ (in 60% aqueous acetone) ($\times 10^6$).	$X{\cdot}OH$ ($\times 10^{10}$).	$X{\cdot}NH_2$ ($\times 10^{10}$).
(Vinyl)	5·5 [1]	—	—	—
Phenyl	6·3 [1]	2·0 [4]	1·3 [5]	3·82 [6]
2-Naphthyl	6·8 [2]	2·8 [4]	2· [5]	1·29 [6]
1-Naphthyl	20·3 [3]	—	—	0·84 [6]
9-Anthryl	22·6 [3]	9·0 [4]	—	—
9-Phenanthryl	—	3·7 [4]	—	—

[1] Dippy, *Chem. Reviews*, 1939, **25**, 206. [2] Derick and Kamm, *J. Amer. Chem. Soc.*, 1917, **39**, 394. [3] Lauder, *Ber.*, 1937, **70**, 1288. [4] This paper (see Experimental). [5] Eisenbrand, *Z. physikal. Chem.*, 1929, *A*, **144**, 441. [6] Hall and Sprinkle, *J. Amer. Chem. Soc.*, 1932, **54**, 3469.

An estimate of the differences in M effects should be obtainable from dipole moments, since these will be determined by the sum of the $-I$ and $\pm M$ effects. From a careful consideration of the moments of 1- and 2-chloronaphthalene, Hampson and Weissberger (*J.*, 1936, 393; cf. Ketelaar and Oosterhout, *Rec. Trav. chim.*, 1946, **65**, 448) deduced that there is a greater mesomeric effect in the 1- than in the 2-naphthyl derivative, but in general the interpretation of dipole moments in polycyclic derivatives is highly complicated owing to vectorial factors (cf. Bergmann and Hershberg, *loc. cit.*; Vassiliev and Syrkin, *Acta Physicochim.*, 1941, **14**, 414).

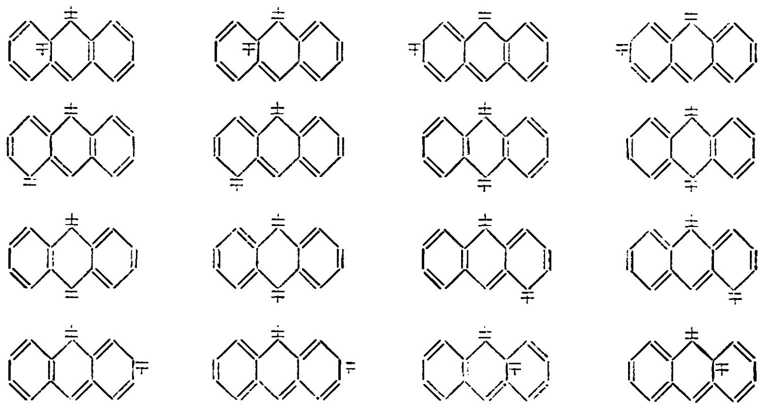
Turning again to the reactivity data in Table III, we see that the estimated differences in the rates of electrophilic substitution of the parent hydrocarbons are considerable and follow the expected sequence of $+T$ effects. In this case, therefore, the latter appear completely to outweigh the $-I$ effects. Amongst the side-chain reactions, the oxotropic rearrangement of the 1-aryl-3-methylallyl alcohols and the neutral hydrolysis of the arylmethyl bromides are facilitated by electron accession (type A; Ingold and Rothstein, *J.*, 1928, 1217), while the prototropic rearrangement of the 1-phenyl-3-arylmethyleneazomethines and the alkaline hydrolysis of the methyl naphthoates require electron recession (type B). As far as can be judged, all four reactions display the expected sequence vinyl $<$ phenyl $<$ 2-naphthyl $<$ 1-naphthyl $<$ 9-anthryl, showing that for these derivatives the $+T$ again outweigh the $-I$ effects in type A reactions. In each case, the differences in rate constants for the different aryl derivatives are remarkably small, in relation both to the effects of other substituents and to nuclear substitution. Thus, oxotropic rearrangement is known to be highly sensitive to substituent effects, *p*-methyl and *p*-methoxyl substituents attached to a phenyl group producing approximately 10- and 100-fold increases in rate, respectively (Braude and Stern, *J.*, 1947, 1096), yet a 9-anthryl as compared with a phenyl substituent only results in an approximately 5-fold increase, and the effects of the other polycyclic substituents studied are even smaller. The same applies to the other side-chain reactions, with the exception of the ammonolysis of aryl acetates where special factors are believed to be involved. The smaller reactivity differences in the side-chain as compared with the nuclear reactions may be due to the fact that, whereas the M effect must necessarily be the same in both types, the additional E effect may be much less prominent in the former than in the latter, as first suggested, in a different connection, by Bird and Ingold (*J.*, 1938, 918). This suggestion is also borne out by comparative data for a *p*-methyl substituent attached to a phenyl group; whereas in oxotropy the rate increase is about 10-fold, it is about 25-fold in nuclear nitration (Benford and Ingold, *J.*, 1938, 929) and about 400-fold in nuclear halogenation (Robertson, Johnston, and De La Mare, *loc. cit.*; Berliner and Bondhus, *J. Amer. Chem. Soc.*, 1946, **68**, 2355; 1948, **70**, 854).

In both side-chain oxotropy and side-chain prototropy, the rates of reaction of the 9-phenanthryl derivatives are unexpectedly small. This is unlikely to be due to any steric effect, since this should be even more pronounced with the 9-anthryl derivative, whereas the reactivity of the latter shows a quantitative linear correlation with the phenyl and naphthyl derivatives (see below), despite the fact that ultra-violet light absorption properties indicate that steric inhibition of resonance occurs in the rearranged isomer (Braude, Fawcett, and Newman, preceding paper). It is of course possible that steric hindrance plays a part in determining the side-chain reactivity of all the polycyclic derivatives, but nevertheless it does not readily explain the *relatively* low reactivity of the 9-phenanthryl derivatives, which therefore appears to be truly electronic in origin. If this deduction be correct, it can have only one explanation, namely, that the M effect of the phenanthryl group is unexpectedly small, smaller than that of the naphthyl and, probably, the phenyl group. In nuclear reactions, where the additional E effect is brought into play, this will not be apparent, but in side-chain reactions, where the E effect is weak, this will result in low reactivity; in type A reactions the $-I$ effect will not be sufficiently compensated by the $+M$ effect, and in type B reactions, the $-I$ effect will not be sufficiently enhanced by the $-M$ effect. The reason for the supposed abnormally small $\pm M$ effect of the phenanthryl group is not clear; it may be due to the two-directional polarisation consequent upon the " angular " arrangement of the benzene nuclei.

(3) *Quantitative Theory.*—(*a*) *Valence-bond method.* A simple approach to a quantitative or semi-quantitative theory of reactivity in polycyclic systems was outlined by Pauling (" The Nature of the Chemical Bond," Cornell, 1940), who pointed out that the reactivities of naphthalene in the 1- and the 2-position can be dicussed in terms of the respective numbers (n) of possible self-polarised structures; 7 self-polarised structures may be written containing a formal charge in the 1-position, and only 6 structures with a formal charge in the 2-position. This treatment can readily be extended to the comparison of the reactivities of different systems; thus $n = 3$

for a phenyl group, $n = 16$ for a 9-anthryl group and $n = 13$ for a 9-phenanthryl group. The 16 structures for a 9-anthryl group are shown below.

Self-polarised resonance structures of anthracene with a formal charge in the 9-position.

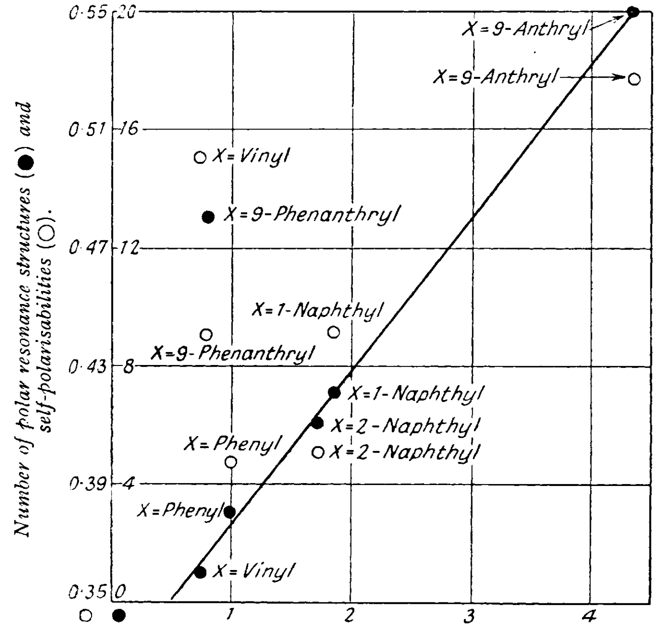


In the unsubstituted parent hydrocarbons, contributions from resonance forms of opposite polarity cancel each other, and the electron density is the same on each carbon atom; but under the influence of an attacking reagent, a particular polarity will be favoured and the polarisability or electromeric effect will be greater, the larger is n. In a substituted hydrocarbon, on the other hand, the substituent will result in a permanent mesomeric polarisation (which appears to be of prime importance in determining side-chain reactivity) and it is reasonable to suppose that, in comparing the effect of the same substituent in different hydrocarbons, the magnitude of the mesomeric effects, as well as of the electromeric effects, will run parallel to n. The quantitative correlation between heterolytic reactivity and the number of possible self-polarised structures depends on the following additional assumptions, amongst others : (1) The contributions of the different self-polarised structures of one system are approximately equal; (2) the excess (or deficiency in) electron-density is proportional to the number of contributing structures carrying a formal charge at a given point; (3) in side-chain reactions the resonance polarisation (mesomeric effect) outweighs any inductive effects. The figure shows a plot of the rate constants for the oxotropic rearrangements of the 1-aryl-3-methylallyl alcohols against n; a straight line is obtained except for the 9-phenanthryl derivative. The value for the corresponding vinyl derivative, 1-vinyl-3-methylallyl alcohol is included for comparison, and falls accurately on the linear plot. On the whole, therefore, the simple valency-bond resonance treatment is very successful in the present case, but it indicates an abnormally small M effect for the 9-phenanthryl group, a conclusion already reached from qualitative considerations. Probably assumptions (1) and (2) do not hold in this case.

A different type of valency-bond treatment, which takes into account contributions from excited (Dewar) structures containing ineffective bonds, has recently been developed by a number of workers (Svartholm, *Arkiv Kemi, Min. Geol.*, 1942, **15**, *A*, 1; Daudel and Pullman, *J. Phys. Radium*, 1946, **7**, 59, 74, 105; Pullman, *Experientia*, 1946, **2**, *A*, 364; Daudel and Daudel, *J. Chem. Physics*, 1948, **16**, 639). The contributions of Dewar-type structures are thought to be considerable, and the density of spin-paired, but ineffectively bonded, π-electrons is expressed as a "*charge totale* or free valency number" (Q), which should be a measure of heterolytic reactivity. The soundness of the underlying mathematical principles has been criticised by Moffitt (*Trans. Faraday Soc.*, 1949, **45**, 373), who calculates a different parameter, the "residual affinity" (r) which is a measure of the initial ease of displacement of an electron on a particular atom (Table V). Both Q and r run parallel, as they theoretically must, to the number n, of self-polarised structures, but the plots of k against Q or r are not linear. The scanty kinetic data so far available, therefore, indicate that contributions from polar structures are more important than contributions from Dewar structures, but further experimental evidence is clearly required on this point.

(*b*) *Molecular-orbital method.* A more elaborate approach to a quantitative theory of reactivity was initiated by Wheland and Pauling (*J. Amer. Chem. Soc.*, 1935, **57**, 2086) and has recently been greatly developed by Coulson and Longuet-Higgins (*Trans. Faraday Soc.*, 1947,

43, 87; *Proc. Roy. Soc.*, 1947, *A*, **191**, 39; **192**, 16; *Sci. J. Roy. Coll. Sci.*, 1948, **18**, 13; *J.*, 1949, 971). Here the electron densities are calculated by the method of molecular orbitals, assuming that the only forces acting on the π-electrons are the exchange forces between paired electrons and the Coulomb fields of the constituent atoms. In unsubstituted aromatic hydrocarbons, the π-electron densities on each carbon atom are unity, but heterolytic reactivity is expressed by the self-polarisabilities (χ) which are a measure of the change in electron density (expressed in terms of the resonance intergral β of a π-electron pair) produced by a change in the electrostatic field.



Relative rates of oxotropic rearrangement of X·CH(OH)·CH:CHMe.

Pauling and Wheland calculated χ for benzene and naphthalene and obtained the values 0·40 (benzene), 0·40 (naphthalene, 1-position) and 0·44 (naphthalene, 2-position). The results of the more refined and extensive calculations of Coulson and Longuet-Higgins are shown in Table V.

TABLE V.

Theoretical quantities related to heterolytic reactivity.

	Number of polar resonance structures (n).	" Charge totale." (Q).[1]	" Self-polar-isabilities" (χ).[2]	" Residual affinities" (r).[3]
(Vinyl)	1	—	0·500	—
Phenyl	3	0·073	0·398	−0·246
2-Naphthyl	6	0·097	0·405	−0·220
1-Naphthyl	7	0·123	0·443	−0·206
9-Phenanthryl	13	—	0·442	—
9-Anthryl	20	0·25	0·526	−0·174

[1] Daudel and Daudel, *J. Chem. Physics*, 1948, **16**, 639. [2] Coulson and Longuet-Higgins, *Proc. Roy. Soc.*, 1947, **192**, *A*, 16; *J.*, 1949, 971; Longuet-Higgins, *Sci. J. Roy. Coll. Sci.*, 1948, **18**, 13. [3] Moffitt, *Trans. Faraday Soc.*, 1949, **45**, 373.

It will be seen that χ again runs parallel, as it theoretically must, to the number n of simple self-polarised structures, but the quantitative relationships are somewhat different for the two parameters. Thus, whereas the values of n indicate, in agreement with experiment, that the difference in heterolytic reactivity between benzene and naphthalene should be greater than the difference in reactivity between the 1- and the 2-position in naphthalene, the values of χ predict the reverse relationship. Again, it seems reasonable to suppose that the polarisability not only of the parent hydrocarbons under the influence of a reagent, but also of the permanent polarisation of a series of hydrocarbon derivatives carrying the same substituent should be directly related to χ. The figure shows that the plot of the rate constants for the oxotropic rearrangements of the 1-aryl-3-methylallyl alcohols against χ departs considerably more from the linear, however, than the plot of k against n. As before, the value of k for the phenanthryl derivative shows a particularly large deviation.

EXPERIMENTAL.

Materials.—The carbinols are described in the preceding paper. The aryl carboxylic acids for dissociation-constant measurements were crystallised from ethanol and had the m. p.s given in parentheses: benzoic (121°), 2-naphthoic (184°), 9-anthroic (217°), and 9-phenanthroic acid (256°). Dioxan and acetone were purified as previously described (Braude, *J.*, 1948, 1971).

Kinetic Measurements.—The technique of kinetic measurements previously described has been further simplified and improved by employing a Beckman DU photoelectric spectrophotometer for the spectrometric assay. This undoubtedly renders the method one of the most convenient and accurate for measuring the rates of organic reactions.

The appropriate amount (10—50 mg.) of carbinol was weighed into a short glass capsule, moistened with one or two drops of dioxan, and added to 25 ml. of reaction medium contained in a special reaction vessel (Part V, *loc. cit.*) immersed in a thermostatically controlled bath. At suitable time intervals, 1 ml. of solution was withdrawn and immediately diluted to 10 or 50 ml. with absolute ethanol and 1 ml. of 0·01M-aqueous potassium hydroxide. The intensity of absorption of the diluted solution at the chosen wave-length was then determined in a 1-cm. cell, the same solvent being used in the comparison cell.

Normally, one of the maxima exhibited by the rearranged carbinol was chosen for intensity determinations. A slightly different procedure had to be adopted in the case of the 9-anthryl derivative, as solutions of the rearranged carbinol are so strongly fluorescent that the maxima do not obey the Beer–Lambert law even at low extinctions (cf. Braude, Fawcett, and Timmons, *J.*, in the press); moreover, the differences in intensities of the maxima of the two isomers are in any case rather small. It was possible, however, to find empirically a wave-length (2650 A.) on a part of the curve at which the intensity was directly proportional to the concentration of rearrangement product and good first-order rate constants were obtained in this way.

Rearrangements of X·CH(OH)·CH:CHMe *in aqueous dioxan*–0·01M-*hydrochloric acid at* **30°.**

c_{ROH} = carbinol concentration (% w/v); c_S = dioxan concentration (% v/v).

(I) X = 1-Naphthyl, c_{ROH} = 0·197, c_S = 60.

Time (mins.)	0	15·0	20·0	25·0	30·0	35·0	420	
$E^{1\%}_{1\,cm.}$ (at 2960 A.)	119	248	279	303	326	345	440	
10^4k (min.$^{-1}$)	—	345	344	341	346	347	—	(Mean) 345

(II) X = 1-Naphthyl, c_{ROH} = 0·192, c_S = 80.

Time (mins.)	0	28·0	45·1	65·0	85·1	106·0	1080	
$E^{1\%}_{1\,cm.}$ (at 2960 A.)	119	221	268	307	340	360	451	
10^4k (min.$^{-1}$)	—	132	132	129	129	123	—	(Mean) 129

(III) X = 2-Naphthyl, c_{ROH} = 0·0365, c_S = 60.

Time (mins.)	0	15·0	23·0	30·2	37·0	45·0	720	
$E^{1\%}_{1\,cm.}$ (at 2455 A.)	123	1040	1410	1640	1855	2010	2600	
10^4k (min.$^{-1}$)	—	310	317	318	323	319	—	(Mean) 318

(IV) X = 2-Naphthyl, c_{ROH} = 0·0360, c_S = 80.

Time (mins.)	0	20·0	40·0	60·0	80·2	100	1080	
$E^{1\%}_{1\,cm.}$ (at 2455 A.)	123	704	1140	1465	1710	1970	2650	
10^4k (min.$^{-1}$)	—	132	128	125	123	129	—	(Mean) 127

(V) X = 9-Anthryl, c_{ROH} = 0·0371, c_S = 60.

Time (mins.)	0	6·1	8·0	10·5	11·5	13·0	100	
$E^{1\%}_{1\,cm.}$ (at 2650 A.)	165	230	246	255	269	281	336	
10^4k (min.$^{-1}$)	—	780	800	785	815	820	—	(Mean) 800

(VI) X = 9-Anthryl, c_{ROH} = 0·0372, c_S = 80.

Time (mins.)	0	10·0	15·0	20·0	26·0	31·0	420	
$E^{1\%}_{1\,cm.}$ (at 2650 A.)	165	207	224	242	255	266	325	
10^4k (min.$^{-1}$)	—	308	308	329	318	321	—	(Mean) 316

(VII) X = 9-Phenanthryl, c_{ROH} = 0·191, c_S = 60.

Time (mins.)	0	20·0	28·0	36·1	45·0	55·0	720	
$E^{1\%}_{1\,cm.}$ (at 3030 A.)	62	174	213	250	277	301	504	
10^4k (min.$^{-1}$)	—	146	149	153	148	147	—	(Mean) 148

(VIII) X = 9-Phenanthryl, c_{ROH} = 0·185, c_S = 80.

Time (mins.)	0	50·0	70·1	90·0	110	130	1080	
$E^{1\%}_{1\,cm.}$ (at 3030 A.)	62	190	230	265	295	321	511	
10^4k (min.$^{-1}$)	—	67·1	66·0	66·1	66·0	66·1	—	(Mean) 66·3

The rate constants were calculated from the expression $k = 2{\cdot}3 \log[(a - x_0)/(a - x)]/t$, where t = time in minutes, x_0 = initial intensity, x = intensity at time t, and a = final intensity at the wave-length chosen. The final intensities a were identical within experimental error ($\pm 2\%$) with the intensities at the same wave-lengths of the pure rearranged carbinols. Some typical runs are reproduced above. The majority of the k values given in Table I are averaged from several runs.

Energies of activation ($E_{\text{Arr.}}$) were computed graphically from the plots of rate constants against $1/T$. The plots were satisfactorily linear. Probability factors refer to specific rate constants (k/c_{A}) and were calculated from the expression $\log A = 0{\cdot}723E_{\text{Arr.}} + \log(k_{30^\circ}/c_{\text{A}}) - 1{\cdot}78$, where c_{A} = acid concentration = 0·01M.

Determination of Dissociation Constants.—The dissociation constants of the aryl carboxylic acids were determined spectrophotometrically in 60% (by vol.) aqueous acetone, bromophenol-blue being used as indicator. (For the general principles of colorimetric and spectrometric acidity measurements, see Brode, *J. Amer. Chem. Soc.*, 1924, **46**, 581; Braude, *J.*, 1948, 1971; Stock and Davies, *J.*, 1949, 1371.) High accuracy was not essential for the present purpose and a simple procedure was adopted in which the hydrogen-ion concentration of suitable carboxylic acid solutions was determined by direct interpolation of the indicator ratios with those of dilute hydrogen chloride solutions. Since the commercial bromophenol-blue employed is not a pure substance and also since it is somewhat unstable in solution, absorption intensities are not recorded in absolute units, but as extinctions (E) of neutral and acid solutions of identical indicator concentrations (*ca.* 0·02%). E values were determined at the maximum (5850 A.) in a 1-cm. cell, a Beckman DU photoelectric spectrophotometer being used. In the following table, E_{N} refers to the neutral solutions and E_{A} to the acid solutions, c is the acid concentration in g.-mols./l., and I is the indicator ratio given by $(E_{\text{N}} - E_{\text{A}})/E_{\text{A}}$.

Acid.	$10^4 c$.	E_{N}.	E_{A}.	I.	10^5 [H$^+$].	f.	$10^6 K_{\text{A}}$.
HCl	0·4	0·715	0·450	0·59	4	—	—
,,	0·6	0·715	0·195	2·7	6	—	—
,,	0·8	0·715	0·121	4·9	8	—	—
,,	1·0	0·715	0·082	7·7	10	—	—
Benzoic	19	1·449	0·330	3·4	6·6	0·90	2·0
2-Naphthoic	10·9	1·449	0·413	2·5	5·8	0·92	2·8
9-Anthroic	5·7	1·463	0·294	3·95	7·1	0·94	9·0
9-Phenanthroic	9·4	1·449	0·364	3·0	6·2	0·92	3·7

On plotting the acid concentration c against I for the hydrochloric acid solutions, a straight line is obtained in the range I = 0·5—5·0 which is also that of highest accuracy in I (Braude, *loc. cit.*). Since hydrogen chloride is almost completely dissociated in 60% aqueous acetone (cf. Braude and Stern, *J.*, 1948, 1978), and since the ionic-strength correction (Stock and Davies, *loc. cit.*) is negligible at the low acid concentrations employed, c_{HCl} can be equated to the hydrogen-ion concentration [H$^+$]. The hydrogen-ion concentration of the carboxylic acid solutions could then be evaluated directly from the I–[H$^+$] plot. The data show that, under the conditions chosen, the carboxylic acids are all less than 15% dissociated and the dissociation constants K_{A} are given by $K_{\text{A}} = f^2[\text{H}^+]^2/(c - [\text{H}^+])$. The activity coefficients f were calculated from the expression $\log f = -1{\cdot}1\sqrt{c}$, based on the limiting Debye–Hückel equation which should be sufficiently applicable at the low ionic strengths involved. The dielectric constant of 60% aqueous acetone at 25° was taken as 48 (Akerlöf, *J. Amer. Chem. Soc.*, 1932, **54**, 4125).

We thank the Department of Scientific and Industrial Research for a Maintenance Grant to one of us (J. S. F.).

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[*Received, October 12th*, 1949.]