# 536. *Mechanism of Aromatic Side-chain Reactions, with Special Reference to the Polar Effects of Substituents. Part XV.* Mesomeric Effects of Elements of the Oxygen Group.*

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Syntheses of *m*- and *p*-methylthio- and -methylseleno-benzaldehydes and -benzoic acids are described. The values of $10^3K = k_2/k_1$ for the equilibria

$$X\cdot C_6H_4\cdot CHO + HCN \underset{k_2}{\overset{k_1}{\rightleftharpoons}} X\cdot C_6H_4\cdot CH(OH)\cdot CN$$

for X = H, *p*-MeO, *p*-MeS, and *p*-MeSe are, respectively, 4·40, 42·9, 38·1, and 35·5 mole l.$^{-1}$. On the basis of the arguments developed by Baker and Hopkins (*J.*, 1949, 1089) these prove that, contrary to earlier postulates, the $+M$ effects of the sixth-group elements decrease in the order O > S > Se. The values of $10^3K$, *viz.*, 4·27, 4·07, and 3·95 respectively, when the same substituents are in the *m*-position, are in the reverse order to that required by the undisturbed operation of the inductive $-I$ effects of the substituents, indicating a second-order relay of the $+M$ effect to this position. The derived order O > S > Se for the ratio $K_p/K_m$ confirms the new order of the $+M$ effects, as also do the values of the dissociation constants, $K_{\text{class}}$, for the corresponding benzoic acids, which have been determined in 30% aqueous alcohol at 25°.

The ultra-violet absorption spectra of these substituted benzoic acids have been plotted in the region 2000—3200 Å for comparison with the corresponding data obtained by Moser and Kohlenberg (*J.*, 1951, 804) for benzoic acids containing other electron-repelling substituents, and the results are shown to be consistent with the order O > S > Se for the $+M$ effects. Proton affinity of OR is also shown to be greater than that of SR, and the general problem of electron release by these two groups is briefly discussed.

WHEN the tautomeric effect of an atom possessing an unshared electron-pair suitably conjugated with an attached unsaturated system was first recognised (Ingold and Ingold, *J.*, 1926, 1310) it was suggested (Ingold, *Chem. Reviews*, 1934, **15**, 237) that the magnitude of such an effect could be correlated with the tendency of the atom to increase its covalency, a rough measure of which would be its ability to co-ordinate a proton and pass into the onium condition. A direct corollary of this early view was that, in any one group of the Periodic Table, the $+T$ effect of such an atom should increase with increasing atomic number since the outer valency electrons would become less and less under the restraint of the positive charge on the central atomic nucleus and so be more deformable the larger the atom. Development of the wave-mechanical treatment of electron behaviour showed that the effect is associated with the delocalisation of the *p*-orbitals of the atom by overlap with the $\pi$-electron orbitals of the attached unsaturated system. Such delocalisation as occurred in the ground state of the molecule was responsible for the permanent polarisation, the mesomeric effect ($+M$), whilst that further delocalisation which could occur in the transition state in reaction gave rise to the corresponding polarisability or electromeric effect ($+E$). The relative magnitudes of such $+M$ and $+E$ effects, however, were still based on the earlier views and hence the series $+M$, F < Cl < Br < I, OR < SR < SeR < TeR, etc., were assumed.

Accumulation of experimental evidence (cf. *inter alia*, Bennett, Brooks, and Glasstone, *J.*, 1935, 1821; Baker and Hopkins, *J.*, 1949, 1089) forced recognition of the reverse order,

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* Part XIV, *J.*, 1949, 1089.

*viz.*, F > Cl > Br > I, for the $+M$ effects of the halogens. It therefore seemed probable that the postulated order for the $+M$ effects of elements in other groups of the Periodic Table might also need reversing, and the present communication provides clear evidence that this is the case for the elements of Group VI.

Baker and Hopkins (*loc. cit.*) called attention to the value of the cyanohydrin equilibrium with substituted benzaldehydes as a reaction which provides clear-cut evidence of the relative magnitudes of the $+M$ effects of groups, and its success in elucidating the order of the $+M$ effects of alkyl and halogen substitutents. Since the groups XMe, where X = O, S, or Se, are of the same general type as the halogens, *i.e.*, they possess (weak) $-I$ and strong $+M$ effects, it was considered that a study of equilibria in the system

$$m\text{- and } p\text{-MeX}{\cdot}C_6H_4{\cdot}CH{:}O + HCN \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{MeX}{\cdot}C_6H_4{\cdot}CH(OH){\cdot}CN$$

should provide conclusive evidence regarding the magnitudes of the $+M$ effects of oxygen, sulphur, and selenium. The argument is essentially of the same type as that employed by Baker and Hopkins (*loc. cit.*) for halogen substituents. Briefly, it is that the extended conjugation between the *p*-substituent, •XMe, the benzene ring, and the aldehyde side-chain in the free aldehyde (conjugation which, in the cyanohydrin, is restricted to the confines of the benzene ring) should stabilise the aldehyde *p*-$MeX{\cdot}C_6H_4{\cdot}CHO$ relative to $C_6H_5{\cdot}CHO$ *more* than it stabilises *p*-$MeX{\cdot}C_6H_4{\cdot}CH(OH){\cdot}CN$ relative to $C_6H_5{\cdot}CH(OH){\cdot}CN$. Hence, with reference to the value of the equilibrium constant $K = k_2/k_1$ for benzaldehyde–benzaldehyde cyanohydrin as standard, a *p*-substituent with a predominant $+M$ effect should increase the value of $K$, and such increase should be greater the larger is its $+M$ effect. In the *m*-position the major operative effect will be the $-I$ effect, upon which may be superimposed any small *second-order* effect due to the inductive relay of real charges which arise from the $+M$ effect. Hence the value of the ratio $K_p/K_m$, in which inductive effects are approximately cancelled out, for the various substituents MeX should be a qualitative measure of the relative magnitudes of the $+M$ effect of X, being larger the greater this effect, and thus confirm any deductions made from the directly observed effect of the substituent in the *p*-position.

Anisaldehyde, *m*-methoxybenzaldehyde, and *p*-methylthiobenzaldehyde are well known. Syntheses of the hitherto unknown methylthio- and methylseleno-benzaldehydes have been achieved by methods described in the Experimental portion of this paper. The general scheme was of the type:

$$NH_2{\cdot}C_6H_4{\cdot}CO_2H \xrightarrow[Na_2S_x \text{ or } KSeCN]{\text{Diazotisation,}} (\text{–X}{\cdot}C_6H_4{\cdot}CO_2H)_2 \xrightarrow[Me_2SO_4]{\text{Zn–NaOH}} \text{MeX}{\cdot}C_6H_4{\cdot}CO_2H \xrightarrow[\text{MeI}]{\text{Ag salt}}$$

$$Y{\cdot}CO_2Me \xrightarrow{NH_2{\cdot}NH_2} Y{\cdot}CO{\cdot}NH{\cdot}NH_2 \xrightarrow{Ph{\cdot}SO_2Cl} Y{\cdot}CO{\cdot}NH{\cdot}NH{\cdot}SO_2Ph \xrightarrow{Na_2CO_3} \text{MeX}{\cdot}C_6H_4{\cdot}CHO$$

(X = S or Se; Y = $MeX{\cdot}C_6H_4{\cdot}$) (cf. McFadyen and Stevens, *J.*, 1936, 584)

The aldehydes were purified through their bisulphite derivatives and semicarbazones as described by Baker and Hemming (*J.*, 1942, 191). Equilibrium constants were determined by using the microtechnique of Baker and Hemming and the results obtained are given in Table 1.

TABLE 1. *Equilibrium constants* K = $k_2/k_1$ *for the reaction* $X{\cdot}C_6H_4{\cdot}CHO + HCN \underset{k_2}{\overset{k_1}{\rightleftharpoons}} X{\cdot}C_6H_4{\cdot}CH(OH){\cdot}CN$ *in constant-boiling alcohol at* 20°. *Catalyst* = 2 *drops* (~0·02 *g.*) *of* $NPr^n_3$ *in* 50 *ml. of a solution initially* 0·2M *with respect to both aldehyde and* HCN.

| | X = | H | MeO | MeS | MeSe |
|---|---|---|---|---|---|
| $10^3K$ mole/l.$^{-1}$ | *p*- | 4·40 ± 0·08 * | 42·9 ± 0·5 | 38·1 ± 0·4 | 35·5 ± 0·7 |
| | *m*- | ,, | 4·27 ± 0·02 | 4·07 ± 0·02 | 3·95 ± 0·03 |
| $10^{-2}$ $\Delta F$ (cals.) | *p*- | 31·63 | $18{\cdot}3_5$ | $19{\cdot}0_4$ | $19{\cdot}4_6$ |
| | *m*- | ,, | $31{\cdot}8_0$ | $32{\cdot}0_8$ | $32{\cdot}2_5$ |
| $K_p/K_m$ | | 1 | 10·05 | 9·36 | 8·98 |

* Previous values 4·47 (Baker and Hemming, *loc. cit.*), 4·45 (Baker and Hopkins, *loc. cit.*).

The value of $10^3K$ for *p*-methoxybenzaldehyde is rather larger than that (31·2) given by Lapworth and Manske (*J.*, 1928, 2533), although that for the *m*-methoxy-compound agrees with their value (4·28).

The conclusion from this evidence is unequivocal. In the *para*-position all three groups greatly increase the value of $K$ relative to that for unsubstituted benzaldehyde, indicating that all these groups have an overall electron-release effect. The order of this increase, $X = O > S > Se$ ($\gg$H) clearly indicates $+M$ effects which decrease in the same order. This is confirmed by the values of $\Delta F$, calculated from the usual relationship $\Delta F = -\boldsymbol{R}T \ln K$, and by the values of the $K_p/K_m$ ratios, which also decrease in the order $X = O > S > Se$ ($>$H).

In the *meta*-position all three substituents exhibit a weak, overall electron-*attraction*, $O < S < Se$, which tends to destabilise the aldehyde relative to its cyanohydrin (Baker and Hopkins, *loc. cit.*). This order is the reverse of that of their $-I$ effects. As a group these substituents fit into their expected place between H and *p*-Cl in the series of increasing electron attraction previously given by Baker and Hopkins (*loc. cit.*, p. 1093), but it is evident that second-order relay of the $+M$ effect from the *m*-position here completely reverses the order of their (weak) $-I$ effects, whereas, in the halogens, it caused only a partial inversion ($Br > Cl > I > F$) of the order of the (stronger) $-I$ effects of these Group VII elements.

*Dissociation Constants of the Acids* $MeX{\cdot}C_6H_4{\cdot}CO_2H$.—The route used for the preparation of the various benzaldehydes involved the intermediate preparation of the corresponding *m*- and *p*-substituted benzoic acids $MeX{\cdot}C_6H_4{\cdot}CO_2H$, and confirmation of the conclusions reached in the study of the cyanohydrin equilibria was sought by determination of the dissociation constants of these acids. Dippy (*J.*, 1937, 1776; *Chem. Reviews*, 1928, **14**, 231) showed that, although the absolute values of the dissociation constants vary greatly according to the solvent used, the relative order of the dissociation constants of a series of acids of closely similar structure is generally unchanged in different solvents, and may safely be used for comparison of the polar effects of a series of substituents in a common parent acid. The combined polar effects of substituents of the $-I$, $+M$ type on the acid strength of the substituted benzoic acid was first discussed by Ingold (*J.*, 1933, 1120) for the case of *p*-anisic acid. He showed that, whilst the $-I$ effect would increase the strength of the acid, the $+M$ effect would weaken it, and the overall electron-release of a *p*-methoxy group, due to the preponderating influence of its $+M$ effect, satisfactorily accounted for the fact that *p*-anisic is a weaker acid than benzoic acid. In the series of acids *p*-$MeX{\cdot}C_6H_4{\cdot}CO_2H$, therefore, we should expect the acid strength to decrease in the order *p*-MeX = (H) > MeSe > MeS > MeO in accordance with the increasing $+M$ effects $Se < S < O$. In the corresponding *meta*-series, since the $+M$ effect can operate, at the most, only as a small second-order effect, whereas the acid-strengthening $-I$ effect can function almost as effectively as it can from the *para*-position, all the acids *m*-$MeX{\cdot}C_6H_4{\cdot}CO_2H$ would be stronger acids than benzoic. The ratios $K_m/K_p$ for the various acids should again be a measure of the relative magnitudes of the $+M$ effects of the atom X.

We have determined the values of $K_{\text{class}}$ at 25·0° in 30% aqueous ethyl alcohol for these acids, a glass electrode being used for the determination of the pH of the solutions. The data are in Table 2. The expectations regarding the strengths of these acids are completely confirmed. As in the cyanohydrin data, the values of both $K_{\text{class}}$ for the *p*-series, and the ratios $K_m/K_p$, reveal a much larger decrease in the value of the $+M$ effect in passing from oxygen to sulphur than from sulphur to selenium. Although the difference in the values of $K_{\text{class}}$ is almost within the experimental error, there is an indication that *m*-methylselenobenzoic acid is a slightly stronger acid than *m*-methylthiobenzoic acid. On the basis of the

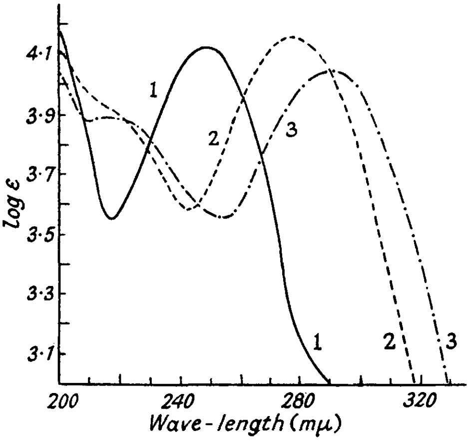
TABLE 2. *Values of* $10^5K^{25}_{\text{class}}$ *for* $MeX{\cdot}C_6H_4{\cdot}CO_2H$ *in* 30 *vol.*% *aqueous* EtOH.

| | MeX = | H | MeO | MeS | MeSe |
|---|---|---|---|---|---|
| $10^5K^{25}_{\text{class}}$ | *p*- | 1·57 | 0·784 | 0·968 | 1·01 |
| | *m*- | 1·57 | 1·93 | $1{\cdot}81_5$ | 1·84 |
| $K_m/K_p$ | | 1 | 2·5 | 1·87 | 1·82 |

undisturbed operation of inductive effects only, the acid strengths in the *meta*-series should decrease in the order *m*-MeO > MeS > MeSe > H and the possible inversion of the positions of sulphur and selenium may indicate the superimposition of a small second-order relay of the mesomeric effect from the *meta*-position in this acid series.

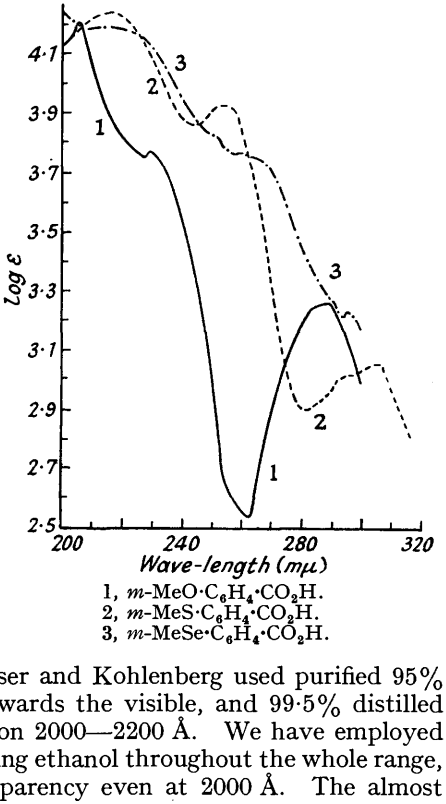
*Ultra-violet Absorption Spectra of the Acids* $MeX{\cdot}C_6H_4{\cdot}CO_2H$.—During our investigations, Moser and Kohlenberg (*J.*, 1951, 804) published data relating to the ultra-violet absorption spectra of some benzoic acids with electron-repelling substituents, including data for *m*- and *p*-anisic acids. The availability of the corresponding methylthio- and methylseleno-benzoic acids has made possible a comparison of the effect of the groups MeO, MeS, and MeSe on the position and intensity of the ultra-violet absorption bands of the substituted benzoic acids in the region from 2000 Å towards the visible, not only amongst themselves, but also with other electron-repelling groups. Moser and Kohlenberg used purified 95% alcohol as a solvent in the region from 2200 Å towards the visible, and 99·5% distilled water + 0·5% of purified 95% ethanol in the region 2000—2200 Å. We have employed 95% of distilled water + 5% purified, constant-boiling ethanol throughout the whole range, since this solvent was found to give >95% transparency even at 2000 Å. The almost complete identity of our results with those of Moser and Kohlenberg for both the position of the absorption maximum and the intensity of the *B*-band of *p*-anisic acid justifies the direct comparison of their results with the new data we now record in Figs. 1 and 2 and in Table 3.

FIG. 1.



1, $p$-$MeO{\cdot}C_6H_4{\cdot}CO_2H$.
2, $p$-$MeS{\cdot}C_6H_4{\cdot}CO_2H$.
3, $p$-$MeSe{\cdot}C_6H_4{\cdot}CO_2H$.

FIG. 2.



1, $m$-$MeO{\cdot}C_6H_4{\cdot}CO_2H$.
2, $m$-$MeS{\cdot}C_6H_4{\cdot}CO_2H$.
3, $m$-$MeSe{\cdot}C_6H_4{\cdot}CO_2H$.

TABLE 3. *Ultra-violet absorption spectra characteristics of* **m**- *and* $p$-$R{\cdot}C_6H_4{\cdot}CO_2H$ *in 5% aqueous* EtOH.

| | *A*-Band | | *B*-Band | | *C*-Band | |
|---|---|---|---|---|---|---|
| R | $\lambda_{max.}$ | log ε | $\lambda_{max.}$ | log ε | $\lambda_{max.}$ | log ε |
| H | 2050 | 4·12 | 2280 | 4·00 | 2710 | 2·88 |
| *p*-MeO | — | — | 2490 | 4·13 | — | — |
| *p*-MeS | ~2120 | 3·95 | 2760 | 4·16 | — | — |
| *p*-MeSe | 2170 | 3·88 | 2900 | 4·05 | — | — |
| *m*-MeO | 2060 | 4·22 | 2300 | 3·76 | 2890 | 3·26 |
| *m*-MeS | 2170 | 4·24 | 2540 | 3·92 | 3025 | 3·05 |
| *m*-MeSe | 2155 | 4·19 | 2600 | 3·77 | 2950 | 3·23 |

~ = Approximate point of inflection.

In the *p*-series, the *C*-band has been obscured, probably by overlap of the very broad *B*-band, whilst the *A*-band appears as only a small peak or a point of inflection. Since, however, Moser and Kohlenberg noted that the shift produced by any substituent is most pronounced and significant in the *B*-band, our attention was concentrated on this range of the spectrum. We accept their conclusion that the *B*- and the *C*-bands correspond to displacements of the 2035- and 2540-Å bands, respectively, of benzene itself. It has been suggested that structural changes which increase the conjugation decrease the energy of excitation and result in a bathochromic shift of the *B*-band, but it is also recognised that inductive effects may change the location of the band. Comparison of the effects of methoxy-, methylthio-, and methylseleno-groups (Table 3) indicates that no single factor is determining such spectroscopic shifts. The increased conjugation resulting from the introduction of these groups in the *p*-position in benzoic acid does cause pronounced bathochromic shifts, coupled with increased intensities, of the *B*-band, but such shift increases in the order MeO $<$ MeS $<$ MeSe. Brand (*J. pr. Chem.*, 1925, **109**, 1) previously observed that the bathochromic shifts (from the ultra-violet to the visible) caused by the introduction of *p*-methylthio-groups into the triphenylcarbonium ion were greater than those produced by similar substitution of methoxy-groups; *e.g.*, *p*-methoxytriphenylcarbonium, $\lambda_{max.}$ 4700; *p*-methylthiotriphenylcarbonium, $\lambda_{max.}$ 5460 Å. In view of our evidence that the $+M$ effects of these groups decrease in the order MeO $>$ MeS $>$ MeSe it would seem fairly certain that such conjugation cannot be the sole factor which determines the magnitude of the bathochromic shift. Because of inadequate knowledge regarding the interplay of factors which contribute to the actual position of the band it seems more reliable to compare the observed shifts with those produced by similarly placed halogen substituents, groups of the same polar type. Such evidence as exists supports the conclusion that, although their $+M$ effects decrease in the order F $>$ Cl $>$ Br $>$ I, the magnitudes of the bathochromic shifts produced by these substituents decrease in the reverse order, *viz.*, Br $>$ Cl $>$ F. Thus Moser and Kohlenberg found, for the *B*-band, in *p*-halogenobenzoic acids : Br, $\lambda_{max.}$ 2400, log $\varepsilon$ 4·10; Cl, $\lambda_{max.}$ 2340, log $\varepsilon$ 4·18. For halogeno-benzenes and -toluenes, Sponer and Teller (*Review Mod. Phys.*, 1941, **13**, 149, 151) give the positions of the 0,0-bands as :

| | PhH | PhCl | PhBr | PhMe | *p*-$C_6H_4MeF$ | *p*-$C_6H_4MeCl$ | *p*-$C_6H_4MeBr$ |
|---|---|---|---|---|---|---|---|
| $\lambda_{max.}$ (Å) ... | 2626 | 2699 | 2703 | 2668 | 2712 | 2755 | 2765 |

Comparison of the data of Price, Tegan, and Walsh (*Discuss. Faraday Soc.*, 1950, No. 9, 54, Fig. 1) for the *B*-bands of fluorobenzene with those of Price and Walsh (*Proc. Roy. Soc.*, 1947, *A*, **191**, 22, Plate 2) for chlorobenzene again shows a greater bathochromic shift by chlorine than by fluorine.

No simple explanation can be offered regarding the effect of MeX substituents in the *meta*-position. In general they exhibit the same trends as those observed by Moser and Kohlenberg for the *m*-substituted acids which they investigated. All three bands suffer a (smaller) bathochromic shift, the magnitude of which is in the order O $<$ Se $<$ S for the *A*- and the *C*-bands, and O $<$ S $<$ Se for the *B*-band. Similar irregularities are exhibited by the values of log $\varepsilon$.

During the progress of these investigations a theoretical treatment of the connection between the size of an atom and its mesomeric effect was published by Baddeley (*J.*, 1950, 663). His explanation, which basically is the same as that previously put forward by Hopkins (Thesis, Univ. Leeds, 1948, p. 135), is that the ratio $R/r$, where $r$ is the single-bond radius of the atom and $R$ is its packing radius, is a semiquantitative measure of the degree of overlap of the *p*-orbital with that of the $\pi$-electrons of the adjacent double bond. For the elements of the oxygen group this clearly indicated an order of decreasing $+M$ effect O $>$ S $>$ Se $>$ Te, which we have now conclusively confirmed experimentally for three of these elements.

Baddeley also called attention to the fact that the ability of an atom to participate in double-bond formation by releasing electrons in the direction of an atom to which it is already covalently attached (*i.e.*, its $+M$ effect) is not directly related to its ability to release electrons in other directions, and cited evidence for his conclusion that " the oxygen atom releases electrons more readily in the direction of its covalent bonds than does the sulphur atom, whereas the latter provides the readier release of electrons in other directions." Some results obtained by one of us (J. W. B.) in collaboration with Mr. W. T. Tweed (Thesis, Univ. Leeds, 1940, p. 50) are relevant to this conclusion.* Using the partition method (Baker, *J.*, 1931, 307) for qualitative assessment of the relative affinities for a proton of phenyl and benzyl ethers and sulphides, we studied the partition of these compounds, under standard conditions, between ligroin and various concentrations of aqueous formic acid, in which acid the compounds dissolve, but from which they may be recovered unchanged by dilution with water. In both the phenyl and benzyl series a much larger proportion of the sulphide than of the corresponding ether was extracted into the ligroin layer, indicating the much smaller affinity of sulphur for a proton. Selected illustrative data, when 100% formic acid was used, are given in Table 4. The much larger diminution in the basic strength between the phenyl and the benzyl compound for the ethers than for the sulphides (*e.g.*, $Ph/Ph{\cdot}CH_2 = 0{\cdot}45$ for O and 0·94 for S) is in harmony with the larger mesomeric conjugation of the oxygen atom with the phenyl group, which will greatly diminish the availability of the *p*-electrons for co-ordination with a proton. Thus oxygen would seem to release electrons *towards a proton* more readily than sulphur. It is common experience, however, that, whereas the stability of onium ions formed by co-ordination with a proton is $R_2\overset{+}{O}H > R_2\overset{+}{S}H$, the reverse order applies in the case of $R_3\overset{+}{O} \ll R_3\overset{+}{S}$ ($R =$ alkyl). Three energy factors are concerned in such formation of onium complexes: †

TABLE 4. *Partition of* ArXR *between ligroin and* 100% *formic acid.*

| Compound | Proportion of ArXR in ligroin layer (%) X = O | X = S | Compound | Proportion of ArXR in ligroin layer (%) X = O | X = S |
|---|---|---|---|---|---|
| PhXMe | 84 | 98 | $PhXPr^i$ | 80 | 96 |
| $Ph{\cdot}CH_2{\cdot}XMe$ | 37 | 92 | $Ph{\cdot}CH_2{\cdot}XPr^i$ | 33 | 88 |

(i) the ionisation potential of the oxygen or sulphur atom,

$$X \longrightarrow X^+ + e \quad (I_O, I_S)$$

(ii) the electron-affinity of the attached group

$$R^+ + e \longrightarrow R \ (R = H \text{ or alkyl}) \ (E_P)$$

(iii) the bond strength of the linkage formed, $^+X{-}H$ or $^+X{-}C$ ($D_{+XH}$, $D_{+XC}$)

For co-ordination of bivalent oxygen or sulphur with a proton we have:

$$-I_O + E_P + D_{+OH} > -I_S + E_P + D_{+SH}$$

*i.e.*,

$$-I_O + D_{+OH} > -I_S + D_{+SH}$$

Owing to the nucleus-screening effect of the inner group of electrons in sulphur, $I_S$ is smaller than $I_O$ and hence, in this case, the order of stability of the different onium complexes is determined mainly by the difference in the strengths of the bonds formed, *i.e.*, $D_{+OH} > D_{+SH}$. For co-ordination with an alkyl group experiment reveals that

$$-I_O + D_{+OC} < -I_S + D_{+SC}$$

The bond strengths $^+O{-}C$ and $^+S{-}C$ are of much more comparable magnitudes than are $^+O{-}H$ and $^+S{-}H$. Hence, in this case, the (reverse) order of stability of the onium complexes is determined mainly by the differences in the ionisation potentials, $I_O > I_S$.

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* The work of Coates (*J.*, 1951, 2003), which appeared after this paper was written, is also of interest in this connection.

† This explanation was suggested to us by Professor M. G. Evans during early discussion of our results.

Such treatment is based on the assumption that a true covalent link is formed between the acceptor atoms and the oxygen or sulphur donor. Lennard-Jones and Pople (*Proc. Roy. Soc.*, 1951, *A*, **205**, 155), in a discussion on hydrogen bonding, have pointed out that lone-pair electrons are distributed in localised points of the molecule and project out in particular directions, and may be regarded as providing regions of negative charge ready to attract positive systems in the neighbourhood. Such interaction may be predominantly electrostatic in character and it is possible that the co-ordination compounds of bivalent oxygen and sulphur with a proton may be of this character, since the formation of a true covalent link would impose a formal positive charge on the highly electronegative oxygen atom. On this view the order of stability, O > S, for these compounds would be expected because of the greater intensity of the negative charge field on the oxygen. If, as seems likely, the co-ordination compounds with alkyl halides involve the formation of a true covalent link between the donor atom and carbon, these compounds would thus contain a different type of linkage and the reverse order of stability, S > O, would then be readily understandable on the lines indicated above.

## EXPERIMENTAL

M. p.s are uncorrected. Analyses are by Drs. Weiler and Strauss, except those marked with an asterisk, which are by Mrs. Y. Richards, the University, Leeds. The large proportions of sulphur and selenium in these compounds seemed to interfere in a rather fortuitous manner with the analyses of some compounds, as the triplicate analyses on the same specimens of *N*-benzenesulphonyl-*N'*-*m*-methylthio- and -*m*-methylseleno-benzoylhydrazide show.

p-*Methoxybenzaldehyde.*—A commerical sample was purified first through its bisulphite compound and then through its semicarbazone, m. p. 203·5°. Regeneration from the purified semicarbazone as described by Baker and Hemming (*loc. cit.*) and distillation in nitrogen gave the pure aldehyde, b. p. 79·5°/0·2 mm.

m-*Methoxybenzaldehyde.*—A commercial sample of *m*-hydroxybenzaldehyde was freed from a small amount of the *p*-isomer by fractional crystallisation from water. The purified *m*-hydroxybenzaldehyde (24 g.) in a solution of sodium hydroxide (10 g.) in water (500 ml.) was shaken with methyl sulphate (19 ml.) for 1 hour. The aldehyde remaining after removal of the ether from the dried ethereal extract had b. p. 78·0°/0·9 mm., after purification through its semicarbazone, colourless leaflets (from aqueous alcohol), m. p. 210° (Found: C, 55·7; H, 5·6; N, 21·8. Calc. for $C_9H_{11}O_2N_3$: C, 55·9; H, 5·7; N, 21·8%).

p-*Methylthiobenzaldehyde.*—*pp'*-Dicarboxydiphenyl disulphide was prepared by treatment of a diazotised solution of *p*-aminobenzoic acid (69 g.) with a solution of sodium polysulphide. prepared by the addition of sodium hydroxide (20 g.) in water (50 ml.) to a hot solution of crystalline sodium sulphide (130 g.) in water (150 ml.) (cf. Thompson, *J. Soc. Chem. Ind.*, 1925, **44**, 196; cf. *Org. Synth.*, Coll. Vol. II, 1st Edn., p. 580, for the corresponding *oo'*-compound). In agreement with the literature the disulphide could be obtained only as an amorphous powder, m. p. 320° (yield, 55 g., 72%).

p-*Methylthiobenzoic Acid.*—The above disulphide (52 g.) was heated under reflux with anhydrous potassium sulphide (32 g.) in alcohol (500 ml.) for 6 hours with mechanical stirring. The dark brown solution was filtered, most of the alcohol (300 ml.) distilled off, the concentrated solution poured into water (1 l.), and the thiol precipitated with hydrochloric acid, filtered off, and methylated by shaking with methyl sulphate (20 ml.) in 2N-sodium hydroxide for 1 hour. Acidification precipitated *p*-methylthiobenzoic acid (50 g., 81%) which crystallised from ligroin (b. p. 60—80°) in colourless leaflets, m. p. 192° (Smiles and Harrison, *J.*, 1922, **121**, 2024, give m. p. 190°) (Found: C, 57·2; H, 4·5. Calc. for $C_8H_8O_2S$: C, 57·1; H, 4·8%). The silver salt of the acid was heated under reflux with methyl iodide (50 ml.) in alcohol (500 ml.) for 6 hours with mechanical stirring. After filtration from the silver residues, which were washed with hot alcohol, the combined alcoholic solutions of the methyl ester were concentrated to 300 ml. and refluxed for 10 hours with 50% hydrazine hydrate solution (50 ml.). Some alcohol (200 ml.) was distilled off and, when cooled, the remaining solution deposited the *hydrazide* (42 g., 83%), colourless needles (from alcohol), m. p. 158° (Found: C, 52·4; H, 5·6; N, 14·8. $C_8H_{10}ON_2S$ requires C, 52·5; H, 5·5; N, 15·3%). The hydrazide (42 g.), dissolved in pyridine (150 ml.), was treated slowly at 0° with benzenesulphonyl chloride (28 ml.), and the solution was kept for 18 hours. Addition of this solution slowly, with rapid stirring, to 20% hydrochloric acid (300 ml.) and crushed ice (200 g.) precipitated N-*benzenesulphonyl*-N'-p-*methylthiobenzoyl*-

*hydrazide* (54 g., 80%), m. p. 237° (decomp.) after repeated recrystallisation from alcohol (Found: C, 52·1; H, 4·2; N, 9·4. $C_{14}H_{14}O_3N_2S_2$ requires C, 52·2; H, 4·4; N, 8·7%). The purified benzenesulphonylhydrazide (45 g.) was steam-distilled from 10% aqueous sodium carbonate (500 ml.) (carbon dioxide stream), and the distillate was extracted with ether. The residue from the dried ethereal extract solidified. Repeated crystallisation from ligroin (b. p. 80—100°) gave *p*-methylthiobenzaldehyde (16·3 g., 71%), m. p. 76° (Gattermann, *Annalen*, 1912, **393**, 225, gives m. p. 78°) (Found: C, 63·3; H, 5·9. Calc. for $C_8H_8OS$: C, 63·2; H, 5·3%). Its semicarbazone crystallised from alcohol in colourless leaflets, m. p. 213° (Gattermann, *loc. cit.*, gives m. p. 213°) (Found: C, 51·2; H, 5·6. Calc. for $C_9H_{11}ON_3S$: C, 51·6; H, 5·3%).

m-*Methylthiobenzaldehyde.*—This was prepared by a similar series of reactions. *m*-Aminobenzoic acid (69 g.) was converted through the disulphide (47 g., 60%), m. p. 242°, into *m*-methylthiobenzoic acid (45 g., 71%), m. p. 126° (in agreement with Smiles and Stewart, *J.*, 1921, **119**, 1795) (Found: C, 57·4; H, 4·8. Calc. for $C_8H_8O_2S$: C, 57·1; H, 4·8%), and its hydrazide, m. p. 85—86° (37 g., 78%). N-*Benzenesulphonyl*-N′-m-*methylthiobenzoylhydrazide* (41 g., 72% yield) had m. p. 167° after crystallisation from alcohol (Found: C, 52·7; 52·1; 52·1*; H, 3·9, 4·6; 4·3*; N, 8·8. $C_{14}H_{14}O_3N_2S_2$ requires C, 52·2; H, 4·4; N, 8·7%). Hydrolysis of this with sodium carbonate afforded m-*methylthiobenzaldehyde* (63%), b. p. 90·0°/0·4 mm. (Found: C, 62·5; H, 5·5. $C_8H_8OS$ requires C, 63·1; H, 5·3%), purified through its *semicarbazone*, m. p. 209° after crystallisation from aqueous alcohol (Found: C, 51·5; H, 5·4; N, 20·4. $C_9H_{11}ON_3S$ requires C, 51·7; H, 5·3; N, 20·1%).

p-*Methylselenobenzaldehyde.*—*pp*′-Dicarboxydiphenyl diselenide, m. p. 295—296° after crystallisation from alcohol, was prepared from *p*-aminobenzoic acid (92 g.) by diazotisation and treatment with potassium selenocyanate by the method of Gaythwaite, Kenyon, and Phillips (*J.*, 1928, 2286), who give m. p. 297°. The diselenide (103 g., 77%) was reduced with zinc dust (36 g.) in a boiling solution of sodium hydroxide (73 g.) in water (500 ml.) and was subsequently methylated with methyl sulphate (58 ml.). The product consisted of only ~50% of the methylselenobenzoic acid which was extracted with boiling benzene, in which the diselenide is insoluble. Gaythwaite, Kenyon, and Phillips (*loc. cit.*) state that the remainder of the product is the diselenide, but we found that repetition of the reduction and methylation of the residue gave only one-tenth of the yield of methylselenobenzoic acid obtained from the original diselenide. The *p*-methylselenobenzoic acid (52 g., 44%) crystallised from ligroin (b. p. 60—80°) as colourless needles, m. p. 175° (in agreement with Gaythwaite *et al.*) (Found: C, 45·8; 44·7*; H, 3·7, 3·65*. Calc. for $C_8H_8O_2Se$: C, 44·7; H, 3·7%). The acid (51 g.) was converted into its silver salt which was esterified as described above (30 ml. of methyl iodide in 300 ml. of alcohol), and the methyl ester was treated, without isolation, with 5% hydrazine hydrate solution (40 ml.), to give the *hydrazide* (22 g., 43%), colourless needles, m. p. 138° after crystallisation from alcohol (Found: C, 42·2; H, 4·4. $C_8H_{10}ON_2Se$ requires C, 41·95; H, 4·4%). Its *benzenesulphonyl* derivative (32 g., 88%) crystallised from alcohol in faintly brown crystals, m. p. 169° (Found: C, 45·4; H, 4·0; N, 7·4. $C_{14}H_{14}O_3N_2SSe$ requires C, 45·5; H, 3·8; N, 7·6%). Hydrolysis of this gave p-*methylselenobenzaldehyde* (14 g., 79%), b. p. 100°/0·5 mm. (Found: C, 48·7; H, 4·3. $C_8H_8OSe$ requires C, 48·3; H, 4·1%), the *semicarbazone* of which, crystallised from aqueous alcohol, had m. p. 215° (Found: C, 42·4*; H, 4·2*; N, 16·2. $C_9H_{11}O_3NSe$ requires C, 42·2; H, 4·3; N, 16·4%).

m-*Methylselenobenzaldehyde.*—The method employed for the *pp*′-diselenide, when applied to *m*-aminobenzoic acid, gave large amounts of selenium from which the required product could not be isolated satisfactorily. The following method, in alkaline solution, gave satisfactory results. *m*-Aminobenzoic acid (75 g.), in concentrated hydrochloric acid (150 ml.) and water (700 ml.), was diazotised with sodium nitrite (36 g.) in water (250 ml.). After 0·5 hour the diazonium solution was added, with rapid stirring, to a solution of potassium selenocyanate (75 g.) in 20% sodium hydroxide (300 ml.). After 2 hours the product was precipitated by addition of hydrochloric acid with rapid stirring, freed from a small amount of selenium, and converted entirely into the diselenide (91 g., 85%) by dissolution in a boiling solution of sodium carbonate (30 g.) in water (700 ml.), boiling for 0·5 hour, and subsequent acidification with hydrochloric acid. Crystallisation from glacial acetic acid gave a product, m. p. 265°, as a light brown, micro-crystalline powder, which, however, seems to be converted into the monoselenide when repeatedly crystallised, because the m. p. falls and the analytical data gradually approximate to those required for the monoselenide [Found: C, 50·6; H, 3·2. Calc. for $C_{14}H_{10}O_4Se$: C, 52·3; H, 3·1. Calc. for $C_{14}H_{10}O_4Se_2$ (diselenide): C, 42·0; H, 2·5%]. Reduction and methylation of the crude diselenide (91 g.) as described for the *p*-compound but extraction of the product with boiling ligroin (b. p. 60—80°) instead of benzene, afforded m-*methylseleno-*

*benzoic acid* (48 g., 48%) which crystallised from ligroin (b. p. 60—80°) in colourless plates, m. p. 121° (Found : C, 45·1 ; H, 3·7. $C_8H_8O_2Se$ requires C, 44·8 ; H, 3·8%). This was converted, by the methods used for the *p*-compound, successively into the *hydrazide* (31 g., 63%) (Found : N, 11·8. $C_8H_{10}ON_2Se$ requires N, 12·1%), which crystallised from water as the *dihydrate*, m. p. 100° (Found : C, 36·6, 36·3 ; H, 5·4, 5·3 ; N, 10·7*. $C_8H_{10}ON_2Se,2H_2O$ requires C, 36·3 ; H, 5·3 ; N, 10·6%), *benzenesulphonylhydrazide* (35 g., 68%), m. p. 158° (Found : C, 45·4, 44·0*, 45·8*, 46·4* ; H, 4·2, 2·7*, 3·6*, 4·2* ; N, 8·2, 7·6*. $C_{14}H_{14}O_3N_2SSe$ requires C, 45·5 ; H, 3·8 ; N, 7·6%), and m-*methylselenobenzaldehyde* (13·6 g., 71%), b. p. 78—79°/0·1 mm., m. p. *ca.* 10° (Found : C, 48·1* ; H, 4·1*. $C_8H_8OSe$ requires C, 48·3 ; H, 4·05%), the *semicarbazone* of which crystallised from aqueous alcohol in needles, m. p. 206° (Found : C, 42·2 ; H, 4·4 ; N, 16·5. $C_9H_{11}ON_3Se$ requires C, 42·2 ; H, 4·3 ; N, 16·4%).

All the aldehydes were regenerated from their highly purified semicarbazones by steam-distillation from 5% oxalic acid in a current of carbon dioxide and were subsequently distilled under reduced pressure (nitrogen) immediately before the setting up of each equilibrium experiment. Not less than five independent determinations of the equilibrium position were made in each case.

For spectroscopic work the benzoic acids were repeatedly recrystallised from ligroin (b. p. 60—80°) to sharp, constant m. p.s recorded above. The constant-boiling alcohol for equilibrium determinations was purified as described by Baker and Hemming (*loc. cit.*), but for spectroscopic investigations this purified sample was further purified by the method of Leighton, Cary, and Schripp (*J. Amer. Chem. Soc.*, 1951, **53**, 2017), the final sample, b. p. 77·5°/751 mm., being stored in the dark.

The catalyst, tri-*n*-propylamine, was a purchased sample, dried over potassium hydroxide and fractionated to give a sample, b. p. 53—54°/20 mm. The hydrogen cyanide solutions were prepared as described by Baker and Hopkins (*loc. cit.*). Equilibrium determinations were made by the micro-methods and with the precautions previously described (Baker and Hemming, *loc. cit.*).

*Strengths of the Substituted Benzoic Acids.*—These were determined in 0·005N-solutions in 30% aqueous alcohol by potentiometric titration with ~0·005N-sodium hydroxide, with a glass electrode in a standard Cambridge pH-meter, benzoic acid itself being examined under the same conditions and all determinations being made at least in duplicate.

*Spectroscopic Data.*—The absorption curves were plotted for 0·0005% solutions of the highly purified acids in a mixture of 95% distilled water and 5% of the highly purified alcohol, a Unicam SP 500 quartz spectrophotometer being employed. A plot of the absorption of the solvent alone showed 95% transparency even at 2000 Å, and duplicate determinations of all spectra were made.

*Partitions* [with W. T. Tweed].—The partition data of the phenyl and benzyl ethers and sulphides between ligroin and 100% formic acid were obtained by the technique previously developed for carbonyl compounds (Baker, *loc. cit.*), except that the decomposition of these ethers and sulphides by cold sulphuric or phosphoric acid rendered the use of these acids as proton donors impossible. The concentration of the ether or sulphide in the ligroin layer was determined refractometrically, since examination of the refractive indices of solutions of known concentrations showed that the plot of concentration against $n^{20}$ gave a straight line. That the retention of the ether or sulphide in the acid layer was due essentially to onium-salt formation was confirmed by observations that, in all samples, the proportion found in the ligroin layer increased as the water content of the formic acid was raised, reaching 100% when the acid was largely diluted.

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