450. *Studies in the Reactivity of Aromatic Hydroxyl Groups. Part III.*

By H. Ll. Bassett and (Miss) A. O'Leary.

Other phenols have now been examined and the following half-periods found for their reaction with acetyl bromide under conditions identical with those of the earlier experiments (J., 1930, 1313; 1931, 2516). The times are given in minutes and the figures in parentheses are the reciprocals of these values compared with that of phenol as unity.

Phenol	14·5	(1)
o-3-Xylenol	37·5	(0·387)
o-4-Xylenol	8·75	(1·657)
m-2-Xylenol	82	(0·177)
m-4-Xylenol	20	(0·725)
m-5-Xylenol	16·5	(0·879)
p-Xylenol	33·5	(0·433)
Mesitol	59·5	(0·244)
Guaiacol	39	(0·372)
Resorcinol monomethyl ether	15	(0·966)
Quinol monomethyl ether	3	(4·833)
Methyl salicylate	very slow	
Methyl *m*-hydroxybenzoate	48	(0·302)
Methyl *p*-hydroxybenzoate	154	(0·094)
Ethyl salicylate	very slow	
Ethyl *m*-hydroxybenzoate	65·75	(0·221)
Ethyl *p*-hydroxybenzoate	206	(0·070)
o-Nitrophenol	very slow	
m-Nitrophenol	170	(0·085)
p-Nitrophenol	470	(0·031)
3-Nitro-*p*-cresol	very slow	
Resorcinol monoacetate	13	(1·115)

Consideration of all the values so far obtained shows that in general the reaction is accelerated by an accession of electrons to, and retarded by a recession of electrons from, the hydroxyl group. In the case of monosubstituted phenols containing a *m*-directing group (NO_2, CO_2Me, CO_2Et) the *m*-compound reacts more rapidly than the *p*-, whereas with an *op*-directing group present (Me, OMe, hal.) the converse is true. This is readily explicable, since the *m*-directing groups will exert their $-I$ effect more strongly from the *p*- than from the *m*-position, leading to a higher rate of reaction for the *m*- than for the *p*-compound, and similarly the $+I$ effect of the methyl group will reverse the relative rates of reaction. In the case of the halogens and methoxyl the $+T$ effect will dominate from the *p*-position, but from the *m*-position there will only be a feeble $-I$ effect, leading to a higher rate of reaction for the *p*-compound.

The greatest interest, however, attaches to the *o*-substituted compounds. These are in each case the slowest in reaction of the three isomerides, but the different substituting groups retard the reaction to very different extents: the order of their efficiency (alkyl$<$OR$<$hal.$<NO_2$, CO_2Me, CO_2Et) is that of their power of attracting electrons. The order also indicates the extent to which chelation occurs in these phenols. The *m*-directing groups make the reaction so slow that it is not possible to differentiate between them.

The only difference between *p*-xylenol and thymol is in the group ortho to the hydroxyl, and thymol reacts slightly more rapidly than *p*-xylenol. On the purely mechanical view it is clearly contrary to expectation that the smaller group should exert the greater steric hindrance, and this point is being further investigated.

The reactions between AcBr and the phenols were carried out in EtOAc at 0° (*loc. cit.*). Three of the carboxylic esters were not sufficiently sol. in EtOAc to permit of the expts. being carried out at the usual concn. and the figures recorded were calculated from results obtained with solutions of half the usual concn., use being made of the ratio of the rates at the two concns. for methyl *m*-hydroxybenzoate.

o-Nitrophenol and methyl and ethyl salicylates reacted so slowly that the half-periods could not be obtained. Even at room temp. they took many days to reach half value.

There was a distinct initial lag in the reaction with guaiacol during the first 10 or 15 min. The reaction was carried out five times with carefully purified material to confirm this.

UNIVERSITY COLLEGE, CARDIFF. [*Received, August* 24*th*, 1932.]