410. *Reactions of αα-Diphenyl-β-picrylhydrazyl with Phenols.*

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Reactions of αα-diphenyl-β-picrylhydrazyl with fourteen phenols have been studied. The results indicate that the phenolic groups are attacked in the step that determines the rates of the reactions. The increases in reactivity towards αα-diphenyl-β-picrylhydrazyl which result from extensions of the system of conjugated double bonds in phenols have been interpreted in terms of a simple molecular-orbital treatment.

The reactions [1-3] of αα-diphenyl-β-picrylhydrazyl with a number of phenols have been found to be of the second order so that

$$-\mathrm{d}[\text{Hydrazyl}]/\mathrm{d}t = k_2[\text{Hydrazyl}][\text{Phenol}]$$

The rate constants for the reactions of αα-diphenyl-β-picrylhydrazyl with a further fourteen phenols have now been measured, and the reaction is discussed in the light of the results.

The measurements were carried out as described previously [1] and the results are given in Tables 1 and 2.

Table 1. *Reactions of phenols with αα-diphenyl-β-picrylhydrazyl in carbon tetrachloride (k is the bimolecular rate constant).*

Phenol	k (l. mole^{-1} min.$^{-1}$)	k (calc.) / k (obs.)
Phenols with a free ortho-*position*		
2-Phenylphenol	9·1 (18·7°)	—
2-Phenyl-4-t-butylphenol	36 (19·2°)	—
4-(α-Methylbenzyl)phenol	77 (19·8°)	1·0
4-(αα-Dimethylbenzyl)-phenol	89 (17·5°)	0·9
2,3-Bis-*p*-hydroxyphenyl-butane	104 (21·8°)	1·5 *
4-Phenylphenol	267 (20·3°)	—
4-Methyl-2-α-methylbenzyl-phenol	506 (19·8°)	1·2
2-Methyl-4-phenylphenol	1500 (18·6°)	—
4-Styrylphenol	6700 (19·8°)	—
4-Cyclohexyl-1-naphthol	~100,000 (20·0°)	—

Phenol	k (l. mole^{-1} min.$^{-1}$)	k (calc.) / k (obs.)
2,6-*Dimethylphenols*		
2,3,5,6-Tetramethyl-phenol	816 (20·3°)	3·0
Pentamethylphenol	5690 (21·1°)	7·7
Phenols with bulky groups in both 2- and 6-positions		
2-Phenyl-6-t-butyl-phenol	36 (19·2°)	—
4,4′-Dihydroxy-3,3′,5,5′-tetra-t-butyl-diphenylmethane	56 (20·3°)	173 *

* Allowance has been made for the presence of two hydroxyl groups.

Table 2. *Rate constants k (l. mole^{-1} min.$^{-1}$) for bimolecular reactions of phenols with αα-diphenyl-β-picrylhydrazyl in benzene and in carbon tetrachloride.*

		In carbon tetrachloride		— In benzene		In benzene at 30° (ref. 2)	
Phenol	$2a$	k	$RT \log_e k + 50a$	k	$RT \log_e k + 50a$	k	$RT \log_e k + 50a$
2-Chlorophenol	—	—	—	—	—	1·2	—
Phenol	1·512	4·3 (18·7°) [1]	38·7	1·3 (16·8°)	38·0	2·3	38·3
2-Methylphenol	—	47 (19·5°) [1]	—	—	—	19	—
4-Phenylphenol	1·437	267 (20·3°)	39·2	57 (17·6°)	38·3	—	—
2-Naphthol	1·455	377 (19·0°) [1]	39·8	132 (17·7°)	39·2	80	39·0
4-Styrylphenol	1·352	6700 (19·8°)	38·9	1600 (19·0°)	38·1	—	—
1-Naphthol	1·341	8000 (15·5°) [1]	38·7	2800 (19·0°)	38·1	3300	38·4

Discussion

McGowan, Powell, and Raw [1] found that the substitution of an alkyl group in the *para*-position of a phenol increased k, the rate constant for its reaction with αα-diphenyl-β-picrylhydrazyl, about 18 times. Each *meta*-alkyl group caused an approximately threefold increase in k and when there was little steric hindrance an *ortho*-alkyl group increased

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[1] McGowan, Powell, and Raw, *J.*, 1959, 3103.

[2] Godsay, Lohmann, and Russell, *Chem. and Ind.*, 1959, 1603.

[3] Venker and Herzmann, *Naturwiss.*, 1960, **47**, 133.

k about eight times. Calculated values of *k* at about 20° and with carbon tetrachloride as solvent were obtained by multiplication of 4·2 (*k* for phenol itself) by these factors. It will be seen from Table 1 that there is again fair agreement between the observed and calculated *k* values provided one *ortho*-position of the phenol is unsubstituted. For such phenols the ratios of calculated to observed values of *k* are near unity. When there are alkyl groups in both the 2- and the 6-position, the value of *k* is less than the calculated value, and the results reported here are in line with those reported previously.[1] It makes little difference whether or not there are hydrogen atoms attached to the α-carbon atom of an alkyl substituent. If such hydrogen atoms were directly involved in the reactions of phenols with αα-diphenyl-β-picrylhydrazyl, the substitution of a phenyl group on the α-carbon atom which carries the hydrogen would be expected to accelerate the reaction considerably. However, the α-methylbenzyl group has almost the same effect on the reaction as the methyl, the t-butyl, and the αα-dimethylbenzyl group. Further, the hydrogen atoms of the aromatic ring of the phenols do not appear to play an important rôle in the reaction because pentamethylphenol behaves normally. Table 2 shows that the reactions are about three times as fast in carbon tetrachloride as in benzene: examples where the reaction is faster in carbon tetrachloride than in toluene and in chloroform have been given.[1]

It might be expected that the αα-diphenyl-β-picrylhydrazyl radical would remove hydrogen from the phenol molecule and yield an aryloxy-radical ArO· as intermediate. It has, however, been suggested [1,4] that the intermediate may be an aryloxy-cation ArO^+ in which case the hydrazyl presumably combines with a hydride ion and yields a radical with a negative charge distributed over the nitro-groups. Whichever intermediate is formed, a relationship might be expected between the rate constants and the values, *a*, of the coefficients of the non-bonding orbitals on the carbon atoms of the methylene groups in the hydrocarbon radicals isoconjugate with the aryloxy-radicals. Longuet-Higgins [5] has given a simple method for the calculation of the non-bonding molecular orbital in alternant hydrocarbon radicals. The squares of these coefficients give the distribution of the odd electron in the radical. The distribution so calculated also gives, to a first approximation, the distribution of charge [6] in both the corresponding cation and anion. Also the structure and resonance energy of a heteroaromatic system are to a first approximation the same as those of the analogous hydrocarbon,[4,7] and Gray and Williams [8] have, for example, used the reactivities of the isoelectronic and more fully investigated radicals $RCH_2\cdot$ when they were considering the reactivities of the radicals RO·. Dewar and Sampson [9] have applied a simplified molecular-orbital method to the hydrolyses of arylmethyl chlorides and give

$$\boldsymbol{R}T \log_e k_2 = -2\beta a + D$$

Here β is the resonance integral between adjacent carbon atoms, which is normally between 20 and 30 kcal.,[9] and *D* is a constant. An equation [1] of this type should apply to the reactions of phenols with αα-diphenyl-β-picrylhydrazyl. For phenol, 4-phenylphenol, 1-naphthol, and 4-styrylphenol, $\boldsymbol{R}T \log_e k + 50a$ is approximately constant (see Table 2) for one solvent and one temperature. The value of $\boldsymbol{R}T \log_e k + 50a$ is however higher for 2-naphthol than for the other phenols. This suggests that a more reactive impurity may have been present in the 2-naphthol, although before use the 2-naphthol was

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[4] McGowan, *J. Appl. Chem.*, 1960, **10**, 312.

[5] Longuet-Higgins, *J. Chem. Phys.*, 1950, **18**, 275.

[6] Longuet-Higgins, *Proc. Chem. Soc.*, 1957, 157; Dewar, "The Electronic Theory of Organic Chemistry," Oxford Univ. Press, 1949, p. 243.

[7] Coulson and Longuet-Higgins, *Proc. Roy. Soc., A*, 1947, **192**, 16; Dewar, *J. Amer. Chem. Soc.*, 1952, **74**, 3341.

[8] Gray and Williams, *Chem. Soc. Special Publ. No.* 9, 1957, p. 97.

[9] Dewar and Sampson, *J.*, 1956, 2789.

recrystallised and converted into its acetate which was recrystallised and hydrolysed to a sample which was again recrystallised.

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[*Received, November* 1*st*, 1960.]