630. *The Rates of Reaction of αα-Diphenyl-β-picrylhydrazyl with Certain Amines and Phenols.*

By J. C. McGowan, T. Powell, and R. Raw.

The reactions of primary arylamines with αα-diphenyl-β-picrylhydrazyl in carbon tetrachloride have been found to obey the third-order law:

Rate of disappearance of hydrazyl = k_3[Hydrazyl]^2[Aniline]

A number of other amines and phenols gave a second-order reaction with the hydrazyl. Alcohols and t-butylamine did not, however, react at an appreciable rate. The effects of substituents on the reaction with phenols are similar to their effects on reactions in which a carbonium ion is formed adjacent to a phenyl ring. Bulky groups *ortho* to the phenolic hydroxyl hinder the reaction. The reactions of *p*-aminobenzonitrile, *m*- and *p*-nitroaniline, *p*-aminobenzophenone, *NN*-dimethyl-*p*-nitroaniline, and *m*- and *p*-nitrophenol were greatly accelerated by light, and were then of first order with respect to αα-diphenyl-β-picrylhydrazyl and of zero order with respect to the amine or phenol.

Braude, Brook, and Linstead [1] found that hydrogen transfer took place between the stable free radical αα-diphenyl-β-picrylhydrazyl and a number of quinols, catechols, hydroaromatic compounds, and aromatic amines. They measured the rates of reactions of the hydrazyl with some hydroaromatic compounds in dioxan, found that the reactions obeyed approximately the third-order law (rate = k_3[Hydrazyl]^2[Donor]), and showed that the energies of activation were between 20 and 35 kcal. per mole. Russell [2] studied the reactions between αα-diphenyl-β-picrylhydrazyl and alkanethiols in benzene and found that the rates of disappearance of the hydrazyl could be expressed as $2k$[Hydrazyl][Thiol]. At 60°, the values of k varied from 0·23 l. mole^{-1} min.$^{-1}$ for t-butanethiol to 4·56 for hexane-1-thiol and the activation energy was in every case about 15 kcal. per mole. The products of the reactions of thiophenol, butanethiol, ammonia, hydrazine, hydroxylamine, methylamine, n-butylamine, isopropylamine, and diethylamine with αα-diphenyl-β-picrylhydrazyl were investigated [3] and in every case high yields of αα-diphenyl-β-picrylhydrazine were obtained. The reactions between αα-diphenyl-β-picrylhydrazyl and some aromatic secondary amines have also been studied.[4,5]

Homolytic transfers of hydrogen atoms from donors to free radicals are of considerable interest in connexion with termination and transfer processes in chain reactions involving radicals. Autoxidations are important examples of such reactions. The propagation reactions are

$$R\cdot + O_2 \longrightarrow RO_2\cdot$$
$$RO_2\cdot + RH \longrightarrow R\cdot O\cdot OH + R\cdot$$

The termination reaction brought about by a hydrogen donor AH is usually considered to be $RO_2\cdot + AH \longrightarrow R\cdot O\cdot OH + A\cdot$. Hammond, Sen, and Boozer,[6] however, consider that this mechanism is incorrect. They found that with *N*-methylaniline and with phenol as inhibitors the initial oxidation rates for cumene and tetralin catalyzed by azodi-isobutyronitrile were inversely proportional to the square roots of the inhibitor concentrations, *i.e.*, the rate of termination was proportional to [Alkylperoxy-radical]^2[Inhibitor]. The reaction therefore resembles the third-order reactions [1] of αα-diphenyl-β-picrylhydrazyl with hydroaromatic compounds. Moreover, no kinetic isotope effect was found when *N*-deutero-*N*-methylaniline and -diphenylamine were compared with the undeuterated

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[1] Braude, Brook, and Linstead, *J.*, 1954, 3574.
[2] Russell, *J. Phys. Chem.*, 1954, **58**, 438.
[3] Brook, Anderson, and Patot, *Canad. J. Chem.*, 1958, **36**, 159.
[4] Hazell and Russell, *Canad. J. Chem.*, 1958, **36**, 1729.
[5] Kuz'minskii and Angert, *Doklady Akad. Nauk S.S.S.R.*, 1954, **96**, 1187.
[6] Hammond, Sen, and Boozer, *J. Amer. Chem. Soc.*, 1955, **77**, 3239.

amines. Hammond, Sen, and Boozer suggest that the alkylperoxy-radicals react reversibly with the inhibitor to give a complex which is then destroyed in an irreversible reaction with a second alkylperoxy-radical. Bickel and Kooyman [7] consider that the usual mechanism is adequate to explain the inhibition of the autoxidation of dihydroanthracene by 2,4,6-trialkylphenols. They [8] treated 4-methyl-2,6-di-t-butylphenol with αα-diphenyl-β-picrylhydrazyl in toluene and found the reaction was of second order: $k = 4{\cdot}7$ and $6{\cdot}3$ l. mole^{-1} min.$^{-1}$ at 20° and 30°, respectively. Some reactions of radicals with hydrogen donors appear to be of second order whilst others are of third order. It is not clear what factors determine the order or the rates of the reactions. αα-Diphenyl-β-picrylhydrazyl is a very convenient radical and since a further study of its reactions with amines and phenols appeared to be worthwhile, the work described below was carried out.

EXPERIMENTAL

αα-Diphenyl-β-picrylhydrazyl, prepared as by Poirier, Kahler, and Benington,[9] was dissolved in carbon tetrachloride. The solution was placed in a three-necked litre flask fitted with a reflux condenser, and carbon dioxide bubbled through it. The flask was placed in a thermostat and when the solution had reached the bath-temperature a weighed quantity of the purified amine or phenol was introduced either alone or in a small amount of carbon tetrachloride, the mixture made up to volume, and the reaction carried out under carbon dioxide. Samples were taken out at intervals and the optical density was measured as quickly as possible in an EEL absorptiometer with Filter No. 604. The concentrations (moles per l.) of αα-diphenyl-β-picrylhydrazyl were found by multiplication of the optical densities for a 1 cm. thick cell by $8{\cdot}58 \times 10^{-5}$. For the slowest reactions, cells 0·5 cm. thick were used, and, for fast reactions, cells 4 cm. or 10 cm. thick. The products were always somewhat coloured and the absorptiometer reading was corrected for this. The reaction was run practically to completion and the colour corresponding to total conversion into the product was obtained. It was then assumed that the same coloured products were produced throughout the reaction in proportion to the amount of αα-diphenyl-β-picrylhydrazyl which had disappeared. Details of two typical runs, one of third order and the other of second order, are given below. $D_{\text{obs.}}$ and $D_{\text{corr.}}$ are the observed and the corrected optical density, the latter being proportional to $(a - x)$, the hydrazyl concentration; $k_2 = x/t(a - x)$, and $k_1 = (1/t) \log_e a/(a - x)$.

m-*Toluidine* ($4{\cdot}900 \times 10^{-3}$ *mol. per l.*) *in carbon tetrachloride at* 40·8° (Cell 4 cm. thick.)

Time (min.)	$D_{\text{obs.}}$	$D_{\text{corr.}}$	10^2k_2	Time (min.)	$D_{\text{obs.}}$	$D_{\text{corr.}}$	10^2k_2	Time (min.)	$D_{\text{obs.}}$	$D_{\text{corr.}}$	10^2k_2
0	0·96	0·96	—	55	0·69	0·62	1·00	210	0·44	0·30	1·05
15	0·86	0·83	1·04	75	0·63	0·54	1·04	385	0·35	0·19	1·05
25	0·80	0·76	1·05	95	0·59	0·49	1·01	1200	0·20	0	—
35	0·76	0·71	1·01	115	0·55	0·44	1·03				

Average : $k_2 = 1{\cdot}03 \times 10^{-2}$

$$k_3 \text{ for third-order reaction} = \frac{x}{(a - x)t} \times \frac{1}{a[m\text{-Toluidine}]}$$

$$= 1{\cdot}03 \times 10^{-2} \times \frac{4}{4{\cdot}900 \times 10^{-3} \times 8{\cdot}58 \times 10^{-5} \times 0{\cdot}96}$$

$$= 1{\cdot}02 \times 10^{5} \text{ l.}^{2} \text{ mole}^{-2} \text{ min.}^{-1}$$

2,4-*Dimethyl*-6-2'-*methylcyclohexylphenol* ($4{\cdot}767 \times 10^{-5}$ *mol. per l.*) *at* 20·0° *in carbon tetrachloride*. The cell used was 4 cm. thick. Results are in Table 1.

$$k \text{ for second-order reaction} = \frac{1}{t} \log_e \frac{a}{a - x} \times \frac{1}{[\text{Phenol}]}$$

$$= 2{\cdot}35 \times 10^{-2} \times \frac{1}{4{\cdot}767 \times 10^{-5}}$$

$$= 493 \text{ l. mole}^{-1} \text{ min.}^{-1}$$

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[7] Bickel and Kooyman, *J.*, 1956, 2215; 1957, 2217.

[8] *Idem, ibid.*, 1957, 2415.

[9] Poirier, Kahler, and Benington, *J. Org. Chem.*, 1952, **17**, 1437.

In Table 2 are given the results of experiments in which primary aromatic amines reacted with αα-diphenyl-β-picrylhydrazyl in carbon tetrachloride solutions. The reactions are all calculated as third order, *i.e.*:

$$\text{Rate of disappearance of hydrazyl} = k_3[\text{Hydrazyl}]^2[\text{Amine}]$$

All the reactions were found to be of the second order with respect to hydrazyl. In a number of cases, different concentrations of amine were used and the reaction was found to be of the first order with respect to the amine: for example, at 41·0° with *p*-chloroaniline at $1{\cdot}570 \times 10^{-2}$ and $7{\cdot}85 \times 10^{-3}$ mole per l., the values of k_3 were $1{\cdot}83 \times 10^4$ and $1{\cdot}87 \times 10^4$ l.^{2} mole^{-2} min.$^{-1}$.

TABLE 1.

Time (min.)	$D_{obs.}$	Corr. D proportional to hydrazyl concn. $(a - x)$	$\frac{10^2}{t} \log_e \frac{a}{a-x}$	Time (min.)	$D_{obs.}$	Corr. D proportional to hydrazyl concn. $(a - x)$	$\frac{10^2}{t} \log_e \frac{a}{a-x}$
0	0·85	0·85 (propl. to a)	—	36	0·40	0·37	2·30
5	0·76	0·755	2·37	41	0·35	0·32	2·38
10	0·68	0·67	2·38	46	0·32	0·29	2·34
15	0·61	0·595	2·38	56	0·26	0·22	2·39
21	0·54	0·52	2·34	116	0·10	0·053	2·39
26	0·48	0·455	2·40	600	0·05	0	—
31	0·44	0·415	2·31			Average =	2·35

TABLE 2. *Reactions of αα-diphenyl-β-picrylhydrazyl with primary aromatic amines.**

Amine	Temp. (°K)	k_3	$RT \log_e k_3$	$14Q$ for Ph group [10]
m-$C_6H_4Cl{\cdot}NH_2$	292·1	$4{\cdot}72 \times 10^2$	3·53	8·0
	314·1	$5{\cdot}70 \times 10^3$	5·36	8·0
	333·1	$9{\cdot}91 \times 10^4$	7·58	8·0
	351·1	$2{\cdot}38 \times 10^5$	8·61	8·0
m-$C_6H_4Br{\cdot}NH_2$	292·6	$5{\cdot}37 \times 10^2$	3·64	7·8
	314·1	$2{\cdot}82 \times 10^3$	4·92	7·8
	332·1	$7{\cdot}74 \times 10^4$	7·40	7·8
	351·1	$2{\cdot}32 \times 10^5$	8·59	7·8
p-$C_6H_4Cl{\cdot}NH_2$	294·6	$2{\cdot}34 \times 10^3$	4·50	7·4
	314·1	$1{\cdot}85 \times 10^4$	6·09	7·4
	332·1	$2{\cdot}72 \times 10^5$	8·23	7·4
	351·1	$1{\cdot}23 \times 10^6$	9·76	7·4
$C_6H_5{\cdot}NH_2$	273·1	$1{\cdot}43 \times 10^3$	3·90	6·6
	294·1	$5{\cdot}91 \times 10^3$	5·03	6·6
	314·1	$6{\cdot}10 \times 10^4$	6·84	6·6
	332·3	$3{\cdot}18 \times 10^5$	8·33	6·6
m-$C_6H_4Me{\cdot}NH_2$	273·1	$2{\cdot}40 \times 10^3$	4·18	6·3
	293·1	$1{\cdot}51 \times 10^4$	5·56	6·3
	313·9	$1{\cdot}01 \times 10^5$	7·14	6·3
p-$C_6H_4Me{\cdot}NH_2$	273·1	$5{\cdot}51 \times 10^3$	4·64	6·2
	293·1	$3{\cdot}70 \times 10^4$	6·02	6·2
	314·1	$2{\cdot}92 \times 10^5$	7·82	6·2

* k_3 = third-order rate constant (l.^{2} mole^{-2} min.$^{-1}$).

TABLE 3. *Reactions of αα-diphenyl-β-picrylhydrazyl with amines.*

Amine	Temp.	k (l. mole^{-1} min.$^{-1}$)	Amine	Temp.	k (l. mole^{-1} min.$^{-1}$)
t-Butylamine ...	76°	<0·0001	Morpholine	77°	1·33
n-Butylamine	77	0·90	*N*-Methylpyrrolidine	76	4·33
Triethylamine ...	40	0·48	Dimethylaniline	40	2·31
	58	0·80		77	5·25
	77	1·62			

In chloroform k for n-butylamine was 0·12 at 20° and 0·37 at 62°.

p-Nitroaniline, *m*-nitroaniline, *p*-aminobenzonitrile, and *p*-aminobenzophenone were found to react with αα-diphenyl-β-picrylhydrazyl only very slowly in the dark but in the light beam of the EEL absorptiometer the reactions all proceeded quite readily. In the light, the reactions were of the first order with respect to αα-diphenyl-β-picrylhydrazyl and of zero order with respect to the amine. The reactions of *NN*-dimethyl-*p*-nitroaniline and *m*- and *p*-nitrophenol with αα-diphenyl-β-picrylhydrazyl were also very slow in the dark and comparatively fast in the light.

[10] McGowan, *J. Soc. Chem. Ind.*, 1949, **68**, 253.

In Table 3 are given results of experiments in which some other amines reacted with αα-diphenyl-β-picrylhydrazyl in carbon tetrachloride. The reactions were all found to be of the first order with respect to the hydrazyl. In the case of morpholine at 77°, the reaction was shown to be of the first order with respect to the amine (*k* was 1·36 at $2{\cdot}10 \times 10^{-2}$ mole per l. and 1·30 at $8{\cdot}06 \times 10^{-2}$ mole per l. of morpholine) and the reactions were assumed to be of the first order with respect to the other amines so that

$$\text{Rate of disappearance of hydrazyl} = k[\text{Hydrazyl}][\text{Amine}]$$

The activation energies for these reactions are about 5 kcal. per mole.

TABLE 4. *Rate constants, k, for the bimolecular reactions of phenols with αα-diphenyl-β-picrylhydrazyl in carbon tetrachloride at about 20° compared with various measures of antioxidant activity and of steric hindrance.*

	1	2	3	4	5	6	7
No phenol	—	—	45	—	0	—	—
Phenols with a free ortho-*position*							
4-Chlorophenol	1·1 (19·0°)	—	45	—	—	—	—
Phenol	4·3 (19·6°)	83	75	0·92	0	1·0	0·25
3,5-Dimethylphenol	46 (20°)	545	—	0·86	25	0·8	—
2-Methylphenol	47 (19·5°)	522	135	0·85	15	0·7	—
4-Methylphenol	55 (19·0°)	291	210	0·84	—	1·4	0·28
4-(1,1,3,3-Tetramethylbutyl)phenol	76 (18·3°)	—	—	—	—	1·0	0·27
4-t-Butylphenol	83 (20·0°)	464	210	0·84	—	0·9	0·20
2,3-Dimethylphenol	100 (18·0°)	591	—	0·85	25	1·0	—
2,5-Dimethylphenol	106 (17·6°)	—	285	0·82	25	1·0	—
β-Naphthol	377 (19·0°)	830	330	0·70	—	—	—
2,4-Di-t-butylphenol	520 (18·0°)	1430	—	0·76	—	1·2	—
2,4-Dimethylphenol	789 (18·4°)	1310	420	0·76	50	0·8	0·19
4-Benzyloxyphenol	7000 (18·0°)	1710	—	0·71	80	—	—
α-Naphthol	8000 (15·5°)	3950	2250	0·68	150	—	—
4-Methoxyphenol	14,000 (21·0°)	—	—	0·71	85	—	0·24
4-Methoxy-3-t-butylphenol	~20,000 (20·8°)	—	—	0·64	150	—	—
4-Methoxy-2-(1,1,3,3-tetramethylbutyl)-phenol	~40,000 (19·5°)	—	—	0·64	295	—	—
4-Methoxy-2,5-di-t-butylphenol	~60,000 (16·0°)	—	—	0·63	160	—	—
4-t-Butylcatechol	>100,000 (18·6°)	—	—	—	—	—	—
4-Methylcatechol	>100,000 (18·0°)	—	—	—	—	—	—
2,6-*Dimethylphenols*							
2,6-Dimethylphenol	117 (19·0°)	1110	420	0·76	30	2·3	0·09
2,4,6-Trimethylphenol	1350 (20·1°)	2070	—	0·67	100	3·6	0·08
2-*Methylphenols with a bulky group in* 6-*position*							
2,4-Dimethyl-6-t-butylphenol	323 (18·5°)	3320	—	0·65	125	15·0	0·04
2,4-Dimethyl-6-(1,1,3,3-tetramethylbutyl)-phenol	350 (19·0°)	—	—	0·66	145	13·8	0·03
2,4-Dimethyl-6-2′-methylcyclohexylphenol	466 (19·3°)	—	—	—	—	10·4	—
Phenols with bulky groups in both 2- and 6-positions							
2,4,6-Tri-t-butylphenol	22 (19·2°)	1430	—	0·69	85	220	0·003
4-Methyl-2,6-di-t-butylphenol	31 (18·3°)	1990	—	0·68	70	156	0·008
4-Ethyl-2,6-di-t-butylphenol	32 (17·0°)	—	—	0·72	105	151	—

In Table 4 are given results of experiments in which phenols were treated with αα-diphenyl-β-picrylhydrazyl in carbon tetrachloride. The rate constants (average) for the bimolecular reactions are given in col. 1. These reactions were carried out at two phenol concentrations, one approximately four times the other, and the values of *k* were always in good agreement.

In col. 2 are shown the relative rates calculated[11] for the capture of tetralyl peroxide radicals at 50° by the phenols. In col. 3 are induction periods found[12] for the oxidation of gasoline containing 0·01% of phenol, in oxygen under pressure at 100°. Col. 4 gives the

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[11] Davies, Goldsmith, Gupta, and Lester, *J.*, 1956, 4926.

[12] Egloff, Morrell, Lowry, and Dryer, *Ind. Eng. Chem.*, 1932, **24**, 1375.

relative oxidation potentials of phenols in 50% alcohol extrapolated to zero pH.[13] Col. 5 gives figures from Penketh [13] for the increase in induction period caused by the addition of 10^{-5}M-phenol to fully saturated petrol in the A.S.T.M. bomb test (D 525 — 49). In col. 6 are the values (see p. 3110) of k(calc.)/k(obs.) for alkyl-phenols, and in col. 7 the differences in wavelength (microns) of the O–H infrared absorption between a dilute solution in carbon tetrachloride and a concentrated solution or melt.[14]

The reactions of some phenols with αα-diphenyl-β-picrylhydrazyl were studied in carbon tetrachloride at temperatures other than around 20° and in other solvents. The results are listed in Table 5 and show that the activation energies are between 5 and 10 kcal. per mole.

TABLE 5. *Further rate constants (k in l. mole^{-1} min.$^{-1}$) for the bimolecular reactions of phenols with αα-diphenyl-β-picrylhydrazyl.*

Phenol	Temp.	Solvent	k	Phenol	Temp.	Solvent	k
p-Cresol	2°	CCl_4	23	2,4,6-Tri-t-butylphenol	1°	CCl_4	9
	39	,,	166		40	,,	46
	77	,,	1015		77	,,	210
	3	$CHCl_3$	7·6				
	18·3	,,	19	4-Methyl-2,6-di-t-butylphenol	1	,,	18
	31	,,	45		19·6	PhMe	17
					32	,,	26
2,4-Dimethyl-6-2′-methylcyclohexylphenol	0	CCl_4	263				

Toluene, sulphur, phthalimide, triphenylmethane, methanol, ethanol, and propan-2-ol did not react at an appreciable rate with αα-diphenyl-β-picrylhydrazyl in carbon tetrachloride at 77°.

DISCUSSION

The effects of charged atoms on the free energies of ionization ($\Delta G_0 = -\boldsymbol{R}T \log_e K$) of protons in acidic molecules and on the free energies of other reactions involving transfers of electrical charges have been discussed elsewhere.[15] Phenyl and other groupings give effects resembling those of charges and each grouping may be allotted an " effective charge " (Q) which may be defined as the hypothetical charge which would be required to give the same effect as the grouping (Y). The following relation may be written for the effect upon a given equilibrium of substitution of different groupings (Y) for hydrogen:

$$\Delta G^\circ = -\boldsymbol{R}T \log_e K = \Delta G_{\mathrm{H}}^\circ + BQ$$

where $\Delta G_{\mathrm{H}}^\circ$ is the value of ΔG° when Y is hydrogen; and B may be equated with $14/2^n$, where n depends on the structure separating the group Y from the atom involved in the change of charge. In the case of the ionization of a proton, it equals the number of atoms between Y and the dissociating proton if all these atoms are saturated, so that with dilute aqueous solutions at 25°

for $\mathrm{YOH} \longrightarrow \mathrm{YO^-} + \mathrm{H^+} \qquad \Delta G^\circ = 19{\cdot}9 - 14Q$

and for $\mathrm{Y{\cdot}NH_3^+} \longrightarrow \mathrm{Y{\cdot}NH_2} + \mathrm{H^+} \qquad \Delta G^\circ = 12{\cdot}9 - 14Q$

The treatment is not confined to 25° and can be applied to other media besides water and for the reactions

$$\mathrm{YO{\cdot}} + \mathrm{e} \longrightarrow \mathrm{YO^-}$$

and $\mathrm{Y{\cdot}\dot{N}H_2^+} + \mathrm{e} \longrightarrow \mathrm{Y{\cdot}NH_2}$

one would expect $\Delta G^\circ = \Delta G_{\mathrm{H}}^\circ - 14Q$.

The effect of groupings and charges upon velocity constants (k) has been found to be similar to the effects upon equilibria, and $\boldsymbol{R}T \log_e k + BQ$ values are constant for

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[13] Penketh, *J. Appl. Chem.*, 1957, **7**, 512.

[14] Sears and Kitchen, *J. Amer. Chem. Soc.*, 1949, **71**, 4110.

[15] McGowan, *Nature*, 1947, **159**, 644; 1951, **168**, 601; *Chem. and Ind.*, 1948, 632; 1951, 601; and ref. 10.

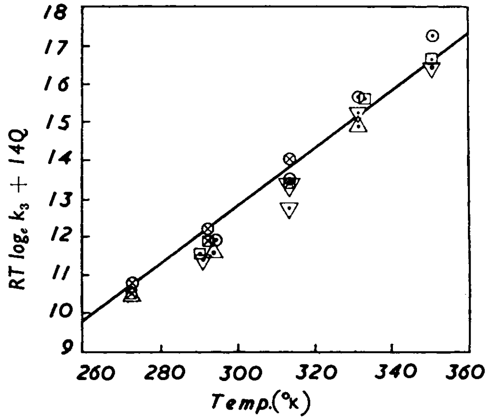
reactions which all involve the same change of charge. The values of Q for substituted phenyl groups listed previously[10] are used here. The equation involving B and Q links reactions in the aromatic series with those in the aliphatic series and indicates the changes in charges more directly than does the well-known equation of Hammett.[16]

The reactions of substituted anilines with αα-diphenyl-β-picrylhydrazyl in carbon tetrachloride have been found to obey the third-order law:

$$\text{Rate of disappearance of hydrazyl} = k_3[\text{Hydrazyl}]^2[\text{Aniline}]$$

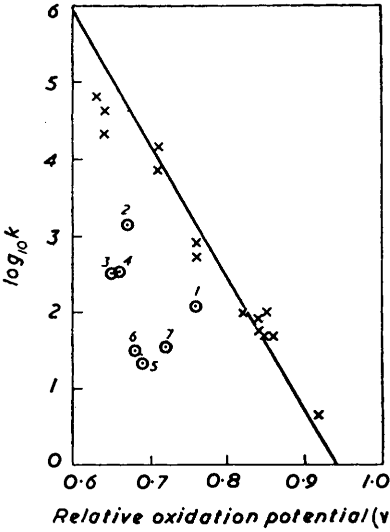
and $\boldsymbol{R}T \log_e k_3 + 14Q$ is a constant for all the anilines at any one temperature. Now if k_3 is equal to $Ae^{-E/\boldsymbol{R}T}$; $\boldsymbol{R}T \log_e k_3 = \boldsymbol{R}T \log_e A - E$ for any one aniline at any temperature; and $\boldsymbol{R}T \log_e k_3 + 14Q - \boldsymbol{R}T \log_e A$ = a constant for all anilines at all temperatures. In Fig. 1, values of $\boldsymbol{R}T \log_e k_3 + 14Q$ are plotted against T and it will be seen that the points fall close to the straight line which corresponds to

FIG. 1. *Reaction of αα-diphenyl-β-picrylhydrazyl with primary aromatic amines.*



⊕ p-CH_3; ○ p-Cl; ⊡ m-Cl; ⊠ m-CH_3; △ H; ▽ m-Br.

FIG. 2. *Relative oxidation potentials and $\log_{10} k$ values for phenols.*



1, 2,6-Dimethylphenol. 2, 2,4,6-Trimethylphenol. 3, 4,6-Dimethyl-1-t-butylphenol. 4, 2,4-Dimethyl-6-(1,1,3,3-tetramethylbutyl)phenol. 5, 2,4,6-Tri-t-butylphenol. 6, 4-Methyl-2,6-di-t-butylphenol. 7, 4-Ethyl-2,6-di-t-butylphenol.

$$\boldsymbol{R}T \log_e k_3 + 14Q = 0{\cdot}075T - 9{\cdot}8 \text{ kcal. mole}^{-1}$$

From this $\log_{10} A = 16{\cdot}4$ l.^{2} mole^{-2} min.$^{-1}$ and $E = 9{\cdot}8 + 14Q$ kcal. mole^{-1}.

Since $\boldsymbol{R}T \log_e k_3$ is a constant for the reactions of αα-diphenyl-β-picrylhydrazyl with anilines under a given set of conditions, the nitrogen atom of the aniline seems to acquire a positive charge in the step of the reaction which controls the rate. Braude, Brook, and Linstead[1] who found that rates of reactions of αα-diphenyl-β-picrylhydrazyl with hydroaromatic compounds obeyed a third-order law, concluded that the reaction involves the reversible association of two of the reacting species followed by attack on this intermediate

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[16] Hammett, *J. Amer. Chem. Soc.*, 1937, **59**, 96: "Physical Organic Chemistry," McGraw-Hill Book Co., New York 1940, Chap. 7.

by a third component. For the aromatic primary amines the transfer of an electron from the amine to the hydrazyl, in the way suggested by Hammond, Sen, and Boozer,[6] seems the most likely mode of association.

$$\text{Hydrazyl} + \text{Ar}\cdot\text{NH}_2 \rightleftharpoons [\text{Hydrazine anion}][\text{Ar}\cdot\text{NH}_2{}^+]$$

The aromatic primary amines give a third-order reaction with αα-diphenyl-β-picrylhydrazyl, but other amines give a second-order reaction. The second-order rate constants reported by Hazell and Russell[4] for 20° in benzene and estimated for 77° by extrapolation of their figures are given below:

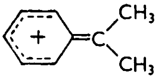
k (l. mole^{-1} min.$^{-1}$)	*N*-Phenyl-*β*-naphthylamine	*N*-Phenyl-α-naphthylamine	Diphenylamine	Methylaniline
At 20°	35	20	3·2	0·29
At 77°	890	291	139	22

These rates are faster than those shown in Table 3. Hazell and Russell[4] found that αα-diphenyl-β-picrylhydrazine was always a major product in their reactions; that tetraphenylhydrazine was formed in 40% yield from diphenylamine; and that triphenylamine did not react at an appreciable rate with αα-diphenyl-β-picrylhydrazyl. It is therefore likely that αα-diphenyl-β-picrylhydrazyl removes a hydrogen atom off the nitrogen in the diarylamines. The results of other workers[5] support this view, although it has been reported[6] that there was no kinetic isotope effect when *N*-deutero-*N*-methylaniline and -diphenylamine were compared with the undeuterated amines. t-Butylamine gives no appreciable reaction with αα-diphenyl-β-picrylhydrazyl and a hydrogen on the α-carbon atom appears to be necessary in aliphatic amines for reaction (see Table 3).

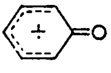
The relative rates[17] (the ratios of the rates for substituted to unsubstituted compound k/k_0) of solvolysis of substituted αα-dimethylbenzyl chlorides in 90% aqueous acetone at 25° are compared below with rates of reaction of the corresponding substituted phenols with αα-diphenyl-β-picrylhydrazyl in carbon tetrachloride at about 20°. The similarity between the figures suggests that the stages which control the rates in the two reactions are very closely related :[15]

	Relative rates k/k_0	
Substituent	Reaction of phenols with αα-diphenyl-*β*-picrylhydrazyl	Solvolysis of dimethylbenzyl chlorides
p-Methoxy	3300	3360
p-Methyl	13	26
p-t-Butyl	19	14
p-Chloro	0·26	0·31

The stage which controls the rate in the solvolysis of the αα-dimethylbenzyl chlorides almost certainly involves the formation of the carbonium ion (I), and so the stage which controls the rate in the reactions of phenols with αα-diphenyl-β-picrylhydrazyl seems to involve the removal of a hydride ion from the phenolic oxygen atom with the formation of an ion (II) with a positive charge. The second electron may be taken up by one of the nitro-groups of the hydrazyl.



(I)



(II)

The introduction of alkyl groups into phenols brings about a big increase in their efficiency as antioxidants.[18] It is therefore of interest that the substitution of alkyl groups in phenols greatly increases the rate of reaction with αα-diphenyl-β-picrylhydrazyl. The

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[17] Brown, Brady, Grayson, and Bonner, *J. Amer. Chem. Soc.*, 1957, **79**, 1897; Brown, Okamoto, and Ham, *ibid.*, p. 1906; Okamoto and Brown, *ibid.*, p. 1909.

[18] Rosenwald, Hoatson, and Chenicek, *Ind. Eng. Chem.*, 1950, **42**, 162; Egloff, Morrell, Lowry, and Dryer, ref. 11.

substitution of any alkyl group in the *para*-position increases the rate about 18 times. Each alkyl group in the *meta*-position increases *k* about three times, and when there is little if any steric hindrance an alkyl group in an *ortho*-position increases *k* about eight times. Calculated values of *k* were obtained by multiplication of 4·2 by these factors. There was fair agreement between the observed and the calculated *k* values provided one *ortho*-position of the phenol is unsubstituted, so that for such phenols the ratio of calculated to observed value of *k* is near unity (Table 4, col. 6). When there are alkyl groups in the 2- and the 6-position, the value of *k* found for the reaction of the phenol with αα-diphenyl-β-picrylhydrazyl is less than the value calculated as described above. The ratio of calculated to observed value of *k* is about three when 2,6-methyl groups are present. This ratio rises to about 15 when there is a 2-methyl group and a bulky alkyl group in the 6-position, and becomes over a hundred when there are bulky groups in both the 2- and the 6-position. It has been found[19] that the smaller the difference between the OH infrared absorption bands (at about 2·7 μ) in a dilute solution and a concentrated solution or melt, the greater the steric hindrance, and figures[14] are given in col. 7 of Table 4 for differences in these wavelengths.

A direct measure of the oxidation–reduction potential of simple phenols is not possible, but indirect measures of the relative oxidation–reduction potentials of phenols have been made.[20] Penketh's results[13] (col. 4, Table 4) for relative oxidation potentials (E_c) at zero pH are plotted against values of $\log_{10} k$ for the reactions of αα-diphenyl-β-picrylhydrazyl with phenols in Fig. 2. The points for phenols with one or no *ortho*-substituents are marked × and the methoxyphenols have been included. These points fall close to the straight line. If the potentials and *k* values were derived from closely related reactions, $-\boldsymbol{R}T \log_e k$ would be expected to equal ($23{\cdot}053E_c$ + a constant) kcal. per mole. This relation would give $(23{\cdot}053/2{\cdot}3026)\boldsymbol{R}T$ for the slope of the $\log_{10} k$ against E_c plot and the line in Fig. 2 has been drawn with this slope. The high values of *k* are only approximate and Penketh claims only an accuracy of ±0·03 v, so that the agreement between the points and the line is as good as could be expected. The points for phenols with two *ortho* groups are marked ⊙ in Fig. 2 and all fall below the line, and the bulkier the groups in the *ortho*-positions the farther below the line do the points fall. Penketh[13] has discussed the relations between his potentials and various other measures of antioxidant activity, so that further discussion here appears to be unnecessary.

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[19] Coggeshall, *J. Amer. Chem. Soc.*, 1947, **69**, 1620.

[20] Conant, *ibid.*, 1926, **48**, 3220; Fieser, *ibid.*, 1930, **52**, 5204.