Sandmeyer Reactions. Part 2.[1] Estimation of Absolute Rate Constants for some Hydrogen-transfer Reactions and for the Transfer of Water Ligands on Cu^{II} to Aryl Radicals by use of a Pschorr Radical Clock

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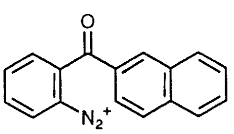
The rate constant for the homolytic Pschorr cyclization of 2-benzoylphenyl radical has been estimated for ambient temperature (20 °C) by competing the cyclization against intermolecular hydrogen-abstractions from alcohols and assuming the latter to occur at rates equal to those measured by Schuler for 4-carboxyphenyl radical. The cyclization was then used as a radical clock for estimating rate constants for other reductions of aryl radicals and for the transfer of water ligands to aryl radicals from Cu^{II}. It is found that sulfate ion inhibits the transfer of water and an explanatory mechanism is proposed.

We have recently described the determination of rate constants for the transfer to aryl radicals of chloride ligands from $[CuCl(OH_2)_5]^+$ and $[CuCl_2(OH_2)_4]$ relative to the transfer of water in solutions of $CuSO_4$ to which sodium chloride had been added and have investigated how the relative rates respond to variation in substitution in the aryl radicals.[1] There appears, however, to have been no successful attempt to determine absolute rate constants for copper-ligand transfers to aryl radicals. Beckwith and co-workers[2,3] calibrated the cyclizations of various 2-(alkenyloxy)phenyl radicals for use as clocks for the timing of the reactions of aryl radicals, but found that these cyclizations proceeded too rapidly for the measurement of the transfer of Cl, Br and CN ligands from Cu^{II} in acetone. Kochi[4] estimated rate constants for the transfer of copper ligands to alkyl radicals by radical clock methods.

Several years ago, Huisgen and Zahler[5] developed the use of the variation in regioselectivity of cyclization of compound **1** to diagnose heterolytic and homolytic pathways in Pschorr cyclization and Cohen and co-workers[6,7] further applied homolytic Pschorr cyclization of 2-benzoylphenyl radical **3** in demonstrating the occurrence of a synthetically useful homolytic route from diazonium ions to phenols *i.e.* a 'hydroxy-Sandmeyer' reaction (Scheme 1). In the latter work, the variation in the ratio of 2-hydroxybenzophenone (**4**) to fluorenone (**6**) produced as a function of change in reaction conditions was examined. The fact that, under appropriate conditions, both the cyclization product **6** and the ligand-transfer product **4** could be observed, suggests that the cyclization of **3** should prove suitable as a radical clock for determining the rate constant for the water ligand transfer and other comparable reactions, provided the rate constant for cyclization can be found.



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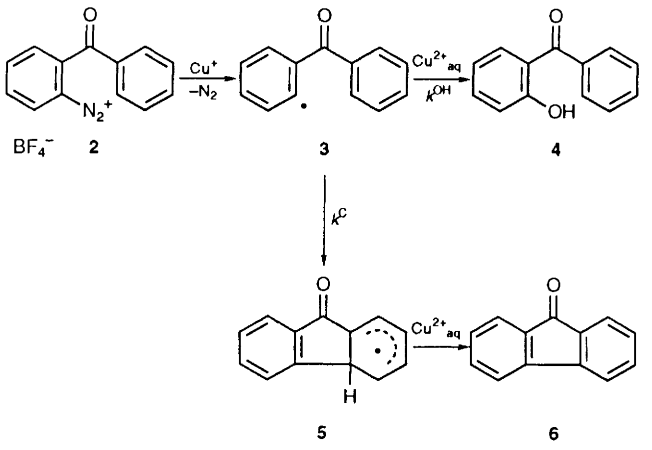
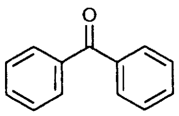
Potential complicating factors would appear to be absent. Thus the cyclization is expected to be irreversible in view of the difference in stabilization between the σ-radical **3** and the delocalized π-radical **5**, and oxidation of **5** to **6** by Cu^{2+}_{aq} is expected to be efficient: cyclohexa-2,4-dienyl radical itself has been reported to be oxidized by Cu^{2+}_{aq} with a rate constant of 3.6×10^6 dm mol^{-1} s^{-1}.[8]



Scheme 1

Here, we report a calibration of the Pschorr cyclization of the 2-benzoylphenyl radical and tests of the validity of the value found for the cyclization rate constant by use of the clock to obtain hydrogen-abstraction rates which could be compared with values for which precedent exists. The clock was then used to determine rate constants for the homolytic transfer of water ligands from Cu^{II}.



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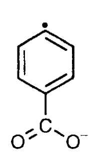

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Results and Discussion

Clock Calibration.—If 2-benzoylbenzenediazonium tetrafluoroborate (**2**) is dissolved in $CuSO_4$ solution and homolysis initiated by addition of a small amount of ascorbic acid, decomposition is immediate. When evolution of nitrogen is complete, the reaction products may be extracted into ethyl acetate and analysed by GLC; they are 2-hydroxybenzophenone (**4**), fluorenone (**6**) and a small amount of benzophenone (**7**). The low yield of **7** (*ca.* 5%) occurs because the ascorbic acid used as initiator, and presumably to some extent **5**, can act as hydrogen donors to the intermediate radical **3**. On addition

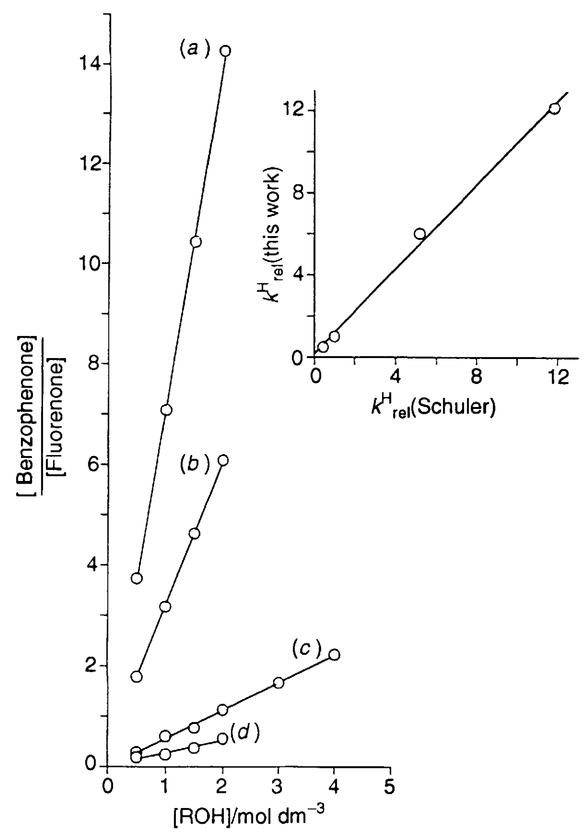

Fig. 1 Dependence of H-transfer to cyclization product ratio, obtained for 2-benzoylphenyl radical, upon the concentration of H-donor alcohol. Inset: H-transfer rate constants (relative to $k^H_{MeOH} = 1$) obtained for 2-benzoylphenyl radical *versus* those obtained for 4-carboxyphenyl radical by Schuler and co-workers (ref. 9). (*a*) Pr^{i}OH; (*b*) EtOH; (*c*) MeOH; (*d*) Bu^{t}OH.

of other hydrogen donors the observed molar ratio of benzophenone to fluorenone increases linearly with the concentration of the donor added. Fig. 1 shows the variation of the product ratio as a function of the concentration of added alcohols. Routine kinetic analysis shows the gradients of the lines in Fig. 1 to be equal to the ratios of the rate constants for H-abstraction from the appropriate alcohol by **3** to that for its cyclization to **5**, *i.e.* k^H/k^C (Table 1).

Schuler and co-workers[9] have reported a pulse-radiolytic study in which rate constants for various reactions of 4-carboxyphenyl radical **8** were measured. These were rate constants for H-abstraction from the same alcohols as we have used relative to that for addition of **8** to 4-bromobenzoate (k^A) and, also, an absolute value for the latter addition, thus allowing evaluation of absolute rate constants for H-abstractions by **8**. In comparing the reactions of **3** and **8**, steric effects of the *ortho*-benzoyl group in **3** might conceivably be relevant. However, if our k^H/k^C values, expressed relative to 1 for MeOH, are plotted against Schuler's k^H/k^A, similarly normalized, a line of unit gradient results (Fig. 1 inset). It seems that any steric factor which might operate in **3** causes no differential effects in the H-abstractions from alcohols in comparison with H-abstractions by **8**. We thus feel justified in assuming that both **3** and **8** abstract hydrogen from the same alcohol at equal rates. Comparison of our values for k^H/k^C with Schuler's values for k^H thus allows an estimation of the cyclization rate of 2-benzoylphenyl radical as 8.0 × 10^5 s^{-1}. Schuler and co-workers estimated errors of ± 10% on their rate constants. Propagating this error with 5% error estimated for our GLC determinations affords (8.0 ± 0.9) × 10^5 s^{-1}.

Table 1 Influence of the concentration of added hydrogen donors (mol dm^{-3}) on the ratio [benzophenone]/[fluorenone] ([**7**]/[**6**]) from homolyses of 2-benzoylbenzenediazonium tetrafluoroborate in aqueous copper sulfate solution

Donor	[**7**]/[**6**]	k^H/k^C (dm^3 mol^{-1})
[Bu^{t}OH]		
0.5	0.188	
1.0	0.245	
1.5	0.369	
2.0	0.553	
		0.244
[MeOH]		
0.5	0.287	
1.0	0.605	
1.5	0.768	
2.0	1.124	
3.0	1.670	
4.0	2.240	
		0.556
[EtOH]		
0.5	1.785	
1.0	3.173	
1.5	4.627	
2.0	6.090	
		2.87
[Pr^{i}OH]		
0.5	3.731	
1.0	7.083	
1.5	10.441	
2.0	14.274	
		6.56
[MeCN]		
0.5	0.160	
1.0	0.232	
1.5	0.334	
2.0	0.402	
3.0	0.537	
		0.152
[THF]		
0.5	5.15	
1.0	9.64	
1.5	13.19	
2.0	16.74	
		7.66
[$H_2P(O)OH$]		
0.1	18.36	
0.15	25.36	
0.20	30.36	
0.25	37.16	
		113.2

Clock Validation.—Having calibrated the benzoylphenyl radical clock, we applied it to the determination of a number of other atom transfer reactions in order to compare the derived values against precedents. Admixture of acetonitrile, tetrahydrofuran and phosphinic acid (hypophosphorous acid) $H_2P(O)OH$, separately, in varying concentrations with **2** in $CuSO_4$ solution exactly as for the alcohols used for calibration, allows relative rate constants k^H/k^C for each of these hydrogen donors to be found (Table 1), and hence their k^H values. The value obtained for k^H_{MeCN} (1.2 ± 0.1) × 10^5 dm^3 mol^{-1} s^{-1}, compares well with the value of (1.04 ± 0.18) × 10^5 dm^3 mol^{-1} s^{-1} found by Scaiano and Stewart[10] for reaction of Ph$^•$ with MeCN in Freon 113 at 298 K. Degrand and Prest[11] have studied the electroreduction of 2-bromobenzophenone in

MeCN in the presence of the nucleophile $PhSe^-$. On the assumption that **3** produced electrochemically, reacts at the diffusion controlled rate (2×10^{10} dm^3 mol^{-1} s^{-1}) with $PhSe^-$, they inferred a first order rate constant for H-abstraction from MeCN by **3** of 4.5×10^7 s^{-1}. If we ascribe neat MeCN (d = 0.786 g cm^{-3}) a molarity of 19.15 mol dm^3, this first order rate constant is converted into a second order constant of 2.3×10^6 dm^3 mol^{-1} s^{-1} (ambient temperature presumed). This seems too large by an order of magnitude; adoption of a rate constant of 1×10^9 dm^3 mol^{-1} s^{-1} for the addition of $PhSe^-$ to **3** would harmonise this result with ours and Scaiano and Stewart's. Our value for k^H_{THF} $(6.1 \pm 0.7) \times 10^6$ dm^3 mol^{-1} s^{-1} is in good agreement with that of Scaiano and Stewart[10] $(4.8 \pm 0.6) \times 10^6$ dm^3 mol^{-1} s^{-1} obtained for reaction of THF with $Ph^•$ in Freon 113 at 298 K.

Although $H_2P(O)OH$ is a well established reagent for reducing diazonium ions synthetically,[12] we have not found a direct precedent for the H-abstraction rate constant. Using the 2-benzoylphenyl radical clock we obtain a value of $(9.0 \pm 1.0) \times 10^7$ dm^3 mol^{-1} s^{-1}. Fu, Bentrude and Griffin[13] competed abstraction of H from $HP(O)(OMe)_2$ by $Ph^•$ with abstraction of Cl from CCl_4 at 60 °C and obtained a relative rate constant $k^H/k^{Cl} = 2.85$. Neglecting any temperature dependence of the selectivity, and solvent differences, combination of this ratio with Scaiano and Stewart's[10] value for k^{Cl} of 7.8×10^6 dm^3 mol^{-1} s^{-1} for Cl-abstraction from CCl_4 by $Ph^•$ in Freon 113 at 298 K, gives a value for $k^H_{HP(O)(OMe)_2}$ of 2.2×10^7 dm^3 mol^{-1} s^{-1}. Thus, when statistical allowance is made for the number of abstractable P–H bonds, our value for $k^H_{H_2P(O)OH}$ is within a factor of *ca.* 2 of a reasonably close precedent. Bridger and Russell[14] competed H-abstraction by $Ph^•$ from Ph_2PH with Cl-abstraction from CCl_4 at 60 °C and obtained a relative rate constant $k^H/k^{Cl} = 60$. Treating this result analogously implies $k^H_{Ph_2PH} = 4.6 \times 10^8$ dm^3 mol^{-1} s^{-1}, a value which is an order of magnitude larger than our statistically corrected value for abstraction from $H_2P(O)OH$. It seems reasonable that the discrepancy be real and relates to the stabilization of $Ph_2P^•$ afforded by delocalization. We have also attempted to estimate the rate constant for transfer of iodine from I_3^- using the 2-benzoylphenyl radical clock. (This was in a copper-free system containing **2**, I_2 and I^- in molar proportions 1:10:100, respectively). However, the rate of transfer proved too great in comparison with the rate of cyclization, even under dilute conditions where the unimolecular process is favoured. Fluorenone was detectable in the product, but its proportion relative to 2-iodobenzophenone was so small that a reliable measure of the product ratio could not be made.

In summary, the 2-benzoylphenyl radical clock, calibrated as described, is suitable for the measurement of reactions of aryl radicals with rate constants in the range 10^5–10^8 dm^3 mol^{-1} s^{-1}. Iodine transfer reactions[15] occur with rate constants 10^9–10^{10} dm^3 mol^{-1} s^{-1} and Beckwith and co-workers[2,3] found that radical clocks, cyclizing at rates suitable for measuring them, were too fast for estimating ligand transfer reactions. It is thus consistent that the 2-benzoylphenyl clock which cyclizes at a rate competitive with water ligand transfer should be too slow for measuring iodine transfer.

Water Ligand Transfer; Counterion Dependence of Reaction Accountability.—Figs. 2(*a*) and (*b*) show the distribution of the products when 2-benzoylbenzenediazonium tetrafluoroborate (**2**) is homolysed in aqueous cupric salt solutions of various concentrations, Fig. 2(*a*) corresponding to the use of $CuSO_4$ and Fig. 2(*b*) to the use of $Cu(NO_3)_2$. It is apparent that, whereas the overall reactant accountabilities are comparable in the two cases, the partitioning between cyclization to give **6** and ligand transfer to give **4** depends upon the counterion. When the counterion is sulfate, the transfer of the water ligand is less efficient, relative to cyclization, than when the counterion is nitrate.

Fig. 3 and Table 2 show the variation in the molar ratio [**4**]/[**6**] *i.e.* R_{obs} as a function of the total copper concentration for both the sulfate and the nitrate salts; points obtained using solutions of $Cu(ClO_4)_2$ were found to lie on the nitrate line. The two lines of Fig. 3 are given [eqns. (1) and (2)], where the quoted uncertainties represent the 95% confidence levels.

For sulfate

$$R_{obs} = (0.852 \pm 0.030)[Cu^{2+}]_t + (0.014 \pm 0.016) \qquad r = 0.9997 \qquad (1)$$

For nitrate/perchlorate

$$R_{obs} = (1.854 \pm 0.077)[Cu^{2+}]_t - (0.010 \pm 0.041) \qquad r = 0.9985 \qquad (2)$$

It was also found that the product ratios are essentially unaffected if KNO_3 is added to $CuSO_4$ solutions but they are reduced if $(NH_4)_2SO_4$ is added to solutions of $CuSO_4$, $Cu(NO_3)_2$ or $Cu(ClO_4)_2$ (Table 2). These observations are consistent with a complexation of Cu^{2+} by SO_4^{2-} to produce a species, or mixture of species, which is less effective at water ligand transfer than $[Cu(OH_2)_6]^{2+}$, the species common to both nitrate and perchlorate solutions.

Hemmes and Petrucci[16] have confirmed that the thermodynamic association constant K_T of $CuSO_4$ in water at 25 °C is 225 ± 20 dm^3 mol^{-1} and have provided evidence that the association process involves the formation, at the diffusion limited rate, of an ion-pair which then collapses in a slower step ($k \sim 10^8$ s^{-1}) where an axial water ligand is replaced by sulfate. In solutions of significant ionic strength, the concentration equilibrium constant K will be less than the thermodynamic value according to $K = K_T\gamma_\pm{}^2$, where $\gamma_\pm$ is the mean activity coefficient of Cu^{2+} and SO_4^{2-}, but the actual values taken for the solution concentrations indicated in Table 2 are unknown.

K is defined by eqn. (3), where subscripts t and e denote total

$$K = \frac{[CuSO_4]_e}{([Cu^{2+}]_t - [CuSO_4]_e)([SO_4^{2-}]_t - [CuSO_4]_e)} \qquad (3)$$

and equilibrium concentrations, respectively, and the aquation of Cu^{2+} is not indicated. Substituting, for convenience, x, y and z for $[Cu^{2+}]$, $[SO_4^{2-}]$ and $[CuSO_4]$, respectively, it is readily shown from this definition that, for the general case

$$z_e = \frac{[K(x_t + y_t) + 1] - \{[K(x_t + y_t) + 1]^2 - 4K^2x_ty_t\}^{\frac{1}{2}}}{2K} \qquad (4)$$

and, for the case of copper sulfate solution where $x_t = y_t$, that

$$z_e = [(2Kx_t + 1) - (4Kx_t + 1)^{\frac{1}{2}}]/2K \qquad (5)$$

and

$$x_e = [(4Kx_t + 1)^{\frac{1}{2}} - 1]/2K \qquad (6)$$

The inhibition of water ligand transfer to **3**, relative to its cyclization, in copper(II) solutions containing sulfate must arise from one of two circumstances: either the sulfatocopper(II) complex is unreactive, in which case the attenuated hydroxylation is brought about solely by the equilibrium concentration of $[Cu(OH_2)_6]^{2+}$ (*i.e.* x_e) or the sulfatocopper(II) complex is reactive but at a rate reduced relative to that of $[Cu(OH_2)_6]^{2+}$ and the attenuated hydroxylation is brought about by the two complexes reacting in parallel.

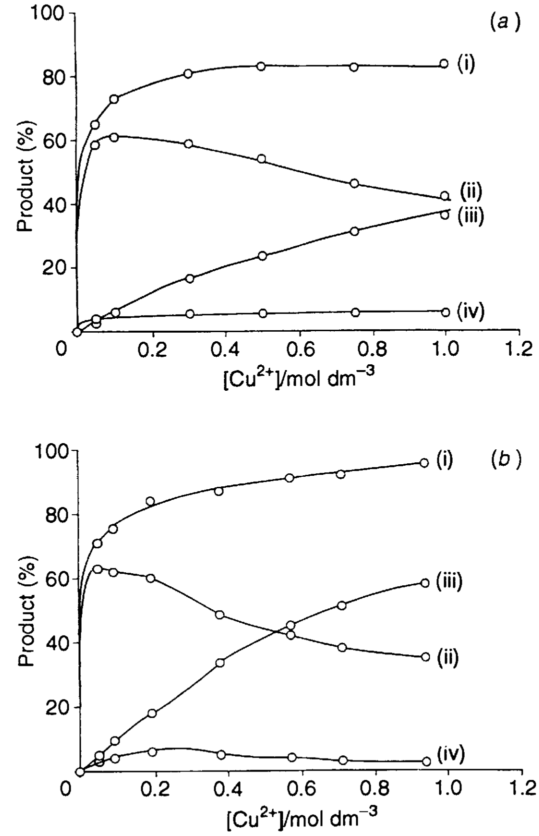

Fig. 2 Percentage distribution of products from the 2-benzoylphenyl radical clock as a function of copper salt concentration (*a*) $CuSO_4$, (*b*) $Cu(NO_3)_2$. (i) Total; (ii) fluorenone; (iii) 2-hydroxybenzophenone; (iv) benzophenone.

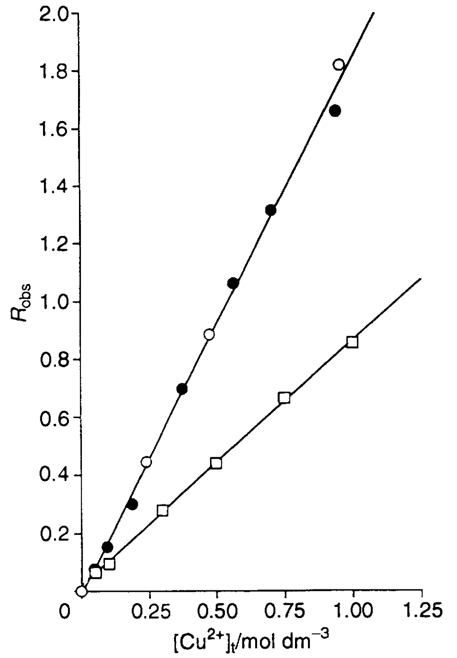

Fig. 3 Variation of water ligand transfer to cyclization product ratio as a function of the total concentration of copper salts: ●, nitrate; ○, perchlorate; □, sulfate

Table 2 The variations in the experimental and calculated product molar ratios R (= [**4**]/[**6**]) as a function of solution composition for the homolysis of 2-benzoylbenzenediazonium tetrafluoroborate in solutions of copper(II) salts

	R_{obs}	R_{calc}[a]
(i) [$CuSO_4$]/mol dm^{-3}		
0.050	0.064	0.057
0.100	0.095	0.105
0.300	0.280	0.281
0.500	0.440	0.451
0.750	0.664	0.659
1.000	0.855	0.864
(ii) [$Cu(NO_3)_2$]/mol dm^{-3}		
0.000	0.000	0.000
0.047	0.076	0.086
0.094	0.153	0.172
0.188	0.301	0.345
0.239[b]	0.444	0.439
0.377	0.696	0.692
0.478[b]	0.884	0.877
0.565	1.062	1.037
0.706	1.313	1.296
0.942	1.657	1.729
0.956[b]	1.817	1.754
(iii) [SO_4^{2-}][c]/mol dm^{-3}		
0.000[d]	1.366	1.376
0.250[d]	1.102	1.114
0.500[d]	0.859	0.860
0.750[e]	0.664	0.659
1.000[f]	0.644	0.600
1.250[f]	0.581	0.588
1.500[f]	0.567	0.583

[a] See text. [b] $Cu(ClO_4)_2$ used. [c] With [Cu^{2+}] = 0.75 mol dm^{-3}. [d] $Cu(ClO_4)_2$ used with added $(NH_4)_2SO_4$. [e] $CuSO_4$ see (i). [f] $CuSO_4$ used with added $(NH_4)SO_4$.

If the first circumstance holds, $R_{obs} = 1.85x_e$ [*cf.* eqn. (2)]. However, eqn. (6) relates x_e to x_t in *non-linear* terms for copper sulfate solution so the observation of the *linear* dependence of R_{obs} on the total copper concentration (x_t) in copper sulfate solution [*cf.* eqn. (1)] implies the first circumstance does not hold, *i.e.* the sulfatocopper complex is not unreactive.*

Since both the aqua- and sulfato-copper complexes hydroxylate **3**, the rate of formation of 2-hydroxybenzophenone, ArOH, is given by eqn. (7), where Ar• ≡ **3**, and k_s^{OH} and k^{OH} are the

$$d[ArOH]/dt = k_s^{OH}[CuSO_4]_e[Ar^\bullet] + k^{OH}[Cu^{2+}]_e[Ar^\bullet] \quad (7)$$

rate constants for the transfer of water ligands from the sulfato- and aqua-complexes, respectively. The rate of cyclization of **3** to fluorenone (Fl) is given by eqn. (8)

$$d[Fl]/dt = k^C[Ar^\bullet] \quad (8)$$

whence

$$\frac{d[ArOH]/dt}{d[Fl]/dt} = (k_s^{OH}/k^C)[CuSO_4]_e + (k^{OH}/k^C)[Cu^{2+}]_e \quad (9)$$

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* By equating $R_{obs} = G_1x_t$ with $R_{obs} = G_2x_e$ and substituting for x_e from eqn. (6), it may be shown that a linear dependence of R_{obs} on both x_t and x_e can occur if K varies inversely with x_t such that $Kx_t = (1 - G_2/G_1)/(G_2/G_1)^2$. No doubt K does decrease as x_t increases due to the increase in intrinsic ionic strength but a specific reciprocal relationship is not expected: it would require K (K_T) to be infinite at infinite dilution whereas several estimates at a relatively low value *ca.* 200 dm^3 mol^{-1} have been reported.[16,17] We therefore conclude that the behaviour of R_{obs} as a linear function of total copper concentration in $CuSO_4$ solution arises because the sulfatocopper(II) is able to hydroxylate **3** and not as a consequence of a medium effect on the copper sulfate equilibrium.

Since the exchange of water and sulfate ligands is very rapid,[16,18] the relative proportions of the two copper species remain constant throughout the reaction and the molar ratio of reaction products, R_{obs}, thus equals the ratio of their rates of formation. Reverting to the earlier notation for concentrations and, for convenience, putting $P = k_s^{OH}/k^C$ and $Q = k^{OH}/k^C$ we get eqn. (10).

$$\begin{aligned} R_{obs} &= Pz_e + Qx_e && (10) \\ &= Pz_e + Q(x_t - z_e) \\ &= Qx_t + (P - Q)z_e && (11) \end{aligned}$$

Substituting for z_e from eqn. (4) gives eqn. (12), which

$$R_{obs} = Qx_t + (P - Q) \times \frac{[K(x_t + y_t) + 1] - \{[K(x_t + y_t) + 1]^2 - 4K^2 x_t y_t\}^{\frac{1}{2}}}{2K} \quad (12)$$

represents a surface in the Cartesian coordinate system having axes R_{obs}, x_t and y_t. The three data sets of Table 2 represent three sections of this surface. We have used the non-linear regression programme SHAZAM [19] to obtain simultaneous fit of the three data sets to the surface, evaluating the best values of P, Q and K: Q is found to be 1.835 ± 0.017, P to be 0.765 ± 0.065 and K to be 104.7 ± 155.0 dm^3 mol^{-1}, respectively, where the uncertainties represent the 95% confidence levels. The value of Q, *i.e.* k^{OH}/k^C, is in agreement, within the respective uncertainties, with the value obtained as the gradient of eqn. (2); the value for P, *i.e.* k_s^{OH}/k^C, is less than Q as required to explain the reduction by sulfate of the rate of hydroxylation of **3** by aquacopper(II); it is also less than the gradient of eqn. (1), consistent with the latter representing the weighted sum of the terms for both the sulfato- and aqua-copper complexes. The value of K, 104.7 dm^3 mol^{-1}, is somewhat less than half of the thermodynamic value and so is of plausible magnitude. However, the very large uncertainty on this figure indicates that it should be regarded as an effective value, representative of a range of values which vary as a function of ionic strength. Much of the uncertainty in K arises because data set (ii) in Table 2 is independent of K. Use of the SHAZAM programme to fit data sets (i) and (iii) only gives $k_s^{OH}/k^C = 0.766 \pm 0.036$, $k^{OH}/k^C = 1.818 \pm 0.035$ and $K = 103.7 \pm 88.2$ dm^3 mol^{-1}, respectively, where the uncertainties are the 95% confidence levels. Thus the values of the parameters obtained are not significantly changed and the uncertainty on K remains large. The use of these estimates in eqn. (12) permits the evaluation of R_{calc} (see Table 2), values of which closely parallel R_{obs}. Since the correlation of R_{calc} with R_{obs} is so good (r = 0.999) and the uncertainties on k_s^{OH}/k^C and k^{OH}/k^C quite small, it is concluded that the value of R_{obs} is rather insensitive to the value of K.

From the relative rate constants gained for water ligand transfer, absolute values can be determined by use of the previously determined value of k^C *i.e.* (8.0 ± 0.9) × 10^5 s^{-1}. Correcting for the numbers of water ligands in the aqua- and sulfato-copper(II) complexes $k_{corr}^{OH} = (1.835 \times 0.017)k^C/6 = (2.45 \pm 0.28) \times 10^5$ dm mol^{-1} s^{-1} and $k_{scorr}^{OH} = (0.765 \pm 0.065)k^C/5 = (1.22 \pm 0.17) \times 10^5$ dm mol^{-1} s^{-1}, where the uncertainties represent the 95% confidence levels; also $(k_s^{OH}/k^{OH})_{corr} = (0.50 \pm 0.05)$. The corrected rate constant for the transfer of a water ligand from the sulfato-copper complex is just one half that for transfer from the aquated ion. It seems reasonable to suggest that in each case the water ligand which is transferred is an axial ligand and the effect of sulfate ligation is merely statistical in halving the number of available axial ligands. Since the exchange processes at Cu^{II} are so rapid,[16,18] exceeding the ligand transfers by a factor of 10^3, any of the water ligands in either complex can be presented to the attacking radical as an axial ligand with equal probability.

Conclusions.—Evidence has been given that the hydrogen-abstractions from alcohols by 2-benzoylphenyl radical are not sterically affected by the 2-benzoyl moiety. On this assumption, comparison of the rate constants for H-abstractions by 2-benzoylphenyl radical relative to its cyclization with absolute rate constants for H-abstraction in the literature, permits evaluation of the cyclization rate constant as (8.0 ± 0.9) × 10^5 s^{-1}.

Use of the cyclization as a radical clock permitted the evaluation of rate constants for the transfer of water ligands from Cu^{II} complexes. The rate constant for transfer from the hexaaquacopper(II) ion was found to be (2.45 ± 0.28) × 10^5 dm^3 mol^{-1} when statistically corrected for the number of water ligands in the complex ion. The presence of sulfate ion was found to inhibit water ligand transfer. The magnitude of the statistically corrected rate constant evaluated for the sulfato-pentaaquacopper(II) complex, (1.22 ± 0.17) × 10^5 dm^3 mol^{-1} s^{-1}, is consistent with the suggestion that the effect of sulfate is merely to reduce the number of axial water ligands available for transfer to the radical.

Experimental

Materials.—2-Benzoylbenzenediazonium tetrafluoroborate (**2**) was prepared by the method of DeTar and Relyea,[20] modified by the use of $NaBF_4$ in place of HBF_4 for the precipitation of the salt. It was purified by dissolution in acetone and reprecipitation by addition of ethoxyethane, m.p. 104–105 °C (decomp.) (Found: C, 51.2; H, 3.3; N, 9.2. $C_{13}H_9BF_4N_2O{\cdot}0.5H_2O$ requires C, 51.2; H, 3.3; N, 9.2%); ν_{max}(tetrachlorobutadiene)/cm^{-1} 1657 (CO) and 2280 (N_2^+); δ_C[$D_2O/(CD_3)_2SO$] 115.7, 130.4, 131.8, 134.9, 135.7, 135.9, 136.2, 137.3, 138.3, 141.9 and 191.8.

Methanol and $CuSO_4{\cdot}5H_2O$ were AnalaR grade; other materials were of reagent grade. Standard master solutions of $CuSO_4$ (1.0 mol dm^{-3}) were made up gravimetrically; master solutions of $Cu(NO_3)_2$ and $Cu(ClO_3)_2$ (*ca.* 1 mol dm^3) were also made up gravimetrically, their accurate concentrations then being determined spectrophotometrically at $\lambda_{max} = 806.5$ nm, calibrating with standard $CuSO_4$ solutions. Solutions of $Cu(ClO_4)_2$ were acidified with a trace of HNO_3 to prevent hydrolysis and turbidity. The more dilute standard copper solutions were prepared volumetrically from such master solutions. Phosphinic (hypophosphorus) acid *ca.* 50% aqueous solution was diluted and standardized titrimetrically using NaOH (0.1 mol dm^3).

Kinetic Measurements.—The following procedure is typical. 2-Benzoylbenzenediazonium tetrafluoroborate (**2**) (120 mg, 4 × 10^{-4} mol) was added to a standard copper salt solution containing, where appropriate, added H-donor or $(NH_4)_2SO_4$ and water to give a combined volume of 49 cm^3 in a 100 cm^3 conical flask. The mixture was efficiently stirred magnetically. When the diazonium salt had dissolved the reaction was initiated by rapid addition of 1 cm^3 aqueous ascorbic acid solution (1 × 10^{-1} mol dm^3). [When $Cu(ClO_4)_2$ was used, some diazonium perchlorate remained in suspension but reacted on initiation.] Evolution of N_2 was immediate and organic products separated. Five minutes after initiation, 10 cm^3 ethyl acetate was added to the flask to dissolve organic products. After separation of the organic phase it was analysed by GLC using a Pye Unicam model PU4500 chromatograph served by a Shimadzu C-R1B integrator; column (1.5 m) 1% DEGA on Gaschrome Q; carrier gas N_2 (*ca.* 40 cm^3 min); temperature 170 °C. The chromatograph was calibrated using standard mixtures of the authentic analytes (benzophenone, 2-hydroxybenzophenone and fluorenone); reaction accountabilities were determined using dibenzofuran as internal standard which was added in the ethyl acetate used to extract the products.

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