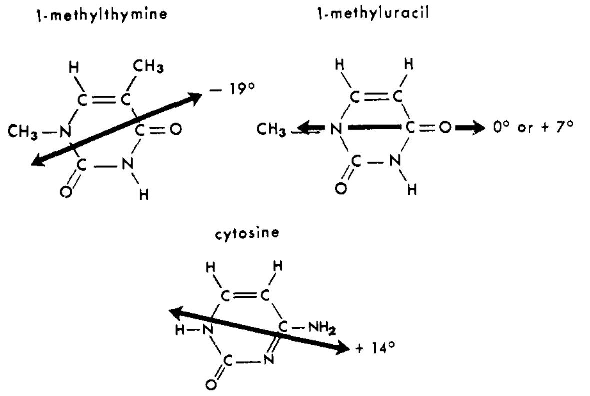

Figure 2. Transition moment directions for the longest wavelength $\pi \rightarrow \pi^*$ transition in 1-methylthymine (all vibronic components),[3] 1-methyluracil (0,0 band),[2] and cytosine monohydrate (0,0 band) as derived from polarized single-crystal absorption measurements. The angles are measured from the N_1-C_4 direction.

like a so-called oriented gas. The absolute intensities and the small Davydov splittings support such a treatment. Assuming that all the intensity in the *c*-axis spectrum is polarized parallel to the molecular planes, the polarization ratio for each vibronic component is consistent with *two* possible in-plane *molecular* directions for the transition moment. These two possible molecular directions are expressed in Figure 1 as the angles, ϕ_1 and ϕ_2, measured relative to the N_1-C_4 direction. Callis and Simpson[1] chose ϕ_1 as the correct alternative on the basis of their results on the 1-methylcytosine crystal. ϕ_1, calculated from the ratio of the *b*- to *c*-polarized intensities for all the vibronic components of the first transition (37,000 to about 41,000 cm^{-1}), is +10°, in excellent agreement with the +9° value estimated from their reflectance data on the (001) face of cytosine monohydrate. However, the best experimental value to be compared with the results of theoretical calculations is $\phi_1 = +14 \pm 1°$ (Figure 1) for the 0,0 band, since this region of the spectrum should be least influenced by intermolecular interactions and molecular vibrations which can "mix" Born-Oppenheimer free-molecule electronic states.

The second transition, centered at about 44,000 cm^{-1} in aqueous solution,[16] dominates the absorption above 42,000 cm^{-1} in the crystal, where the polarization ratio levels off at about 8.5:1. This polarization ratio corresponds to a ϕ_1 of $-5 \pm 3°$, again in good agreement with the Callis and Simpson result of $-1 \pm 10°$.

Figure 2 summarizes the experimentally determined transition moment directions for the first $\pi \rightarrow \pi^*$ transition in the three common nucleic acid pyrimidines. Theoretically predicted directions for uracil and thymine,[17-21] including a recent *ab initio* calculation on thymine,[22] are generally within about 10° of the observed directions for 1-methyluracil[2] and 1-methylthymine.[3] However, π-electron calculations on cytosine, which require more extensive parameterization than uracil or thymine because of the greater variety of chemical bonds, predict directions which generally differ from experimental values by about 60°;[16-21,23] the maximum possible difference between theory and experiment is 90°.

The good agreement between the transition moment directions calculated from the reflectance data for the (001) crystal face, which is nearly parallel to the molecular planes, and our absorption data for the (100) crystal face support the assumption in the previous analysis that all of the *c*-axis intensity is polarized parallel to the molecular planes. Unlike the case of 1-methyluracil, where we obtained a spectrum polarized almost exactly perpendicular to the molecular planes,[2] we cannot locate $n \rightarrow \pi^*$ transitions below 44,000 cm^{-1} in cytosine monohydrate. Rich and Kasha found an $n \rightarrow \pi^*$ transition at about 36,000 cm^{-1} in polycytidylic acid from polarized absorption measurements on oriented films.[24] If an $n \rightarrow \pi^*$ transition in cytosine monohydrate were of comparable energy, intensity, and polarization we would have observed it as a distinct band in the *c*-axis polarized spectrum.

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[25] Department of Chemistry, The City College of the City University of New York, New York, N. Y. 10031.

Thomas P. Lewis,*[25] William A. Eaton*
Laboratories of Molecular Biology and Physical Biology
National Institute of Arthritis and Metabolic Diseases
National Institutes of Health, Bethesda, Maryland 20014
Received January 11, 1971

Reversible Addition of Benzoyloxy Radicals to Benzene

Sir:

Irradiation of benzoyl peroxide or benzil in benzene in the presence of oxygen gives phenyl benzoate[1,2] in yields which increase with oxygen concentration. These observations have been accounted for by assuming that the addition of benzoyloxy radicals to benzene is reversible, Scheme I.[1,2] This reversible addition provides the only analogy in free-radical chemistry for the suggestion that the major path of deactivation in benzene of carbonyl triplet states with n,π^* electronic character involves reversible formation of adduct biradicals.[3-6] In the following, evidence is pre-

Scheme I. The Fate of Benzoyloxy Radicals in Benzene

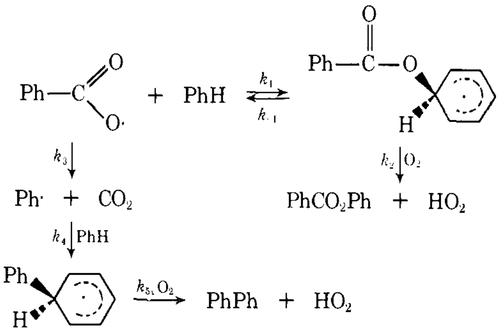

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Table I. Product Yields from the Photochemical Decomposition of Benzoyl Peroxide in Benzene at 30° [a]

O_2, $M \times 10^3$	Biphenyl	Phenyl benzoate	Benzoic acid
0	66[b]	13	46
1.5	31	40	29
3.6	14	54	40
7.2[c]	10	58	40
7.2[d]	7.6	48	48

[a] Yields are reported as (100 mol of product)/(moles of peroxide consumed); benzoyl peroxide concentrations are 4.1×10^{-3} *M* unless otherwise noted. [b] Sum of biphenyl and dihydrobiphenyls. Biphenyl/dihydrobiphenyl = 2.98. [c] Average of three independent determinations. [d] Benzoyl peroxide concentration 2.2×10^{-2} *M*.

Table II. Isotopic Compositions of Phenyl Benzoate and Biphenyl Obtained Using C_6H_6–C_6D_6 as Solvent[a]

		Isotopic composition, %[c]			
Product	O_2, $M \times 10^3$ [b]	d_0	d_4	d_5	d_{10}
Phenyl benzoate	1.5[d]	84.2 ± 0.7	1.2 ± 0.1	14.6 ± 1.1	
Biphenyl		53.1 ± 0.3	2.6 ± 0.2	43.8 ± 0.4	0.6 ± 0.1
Phenyl benzoate	7.2[e]	75.7 ± 0.1	1.4 ± 0.1	22.9 ± 0.1	
Biphenyl		53.9 ± 0.7	2.3 ± 0.2	43.1 ± 0.5	0.7 ± 0.05

[a] Benzoyl peroxide 0.1 *M*. [b] See footnote 8. [c] Ranges indicate reproducibility. The actual errors in the minor components can be considerably higher. [d] Benzene composition 50.0 ± 0.5% d_0, 3.1 ± 0.4% d_5, 46.9 ± 0.8% d_6; product yields biphenyl, 32%; phenyl benzoate, 27%. [e] Benzene composition 48.9 ± 0.3% d_0, 1.9 ± 0.1% d_5, 49.2 ± 0.3% d_6; product yields biphenyl, 13%; phenyl benzoate, 46%.

sented which substantiates the reversible addition of benzoyloxy radicals to benzene.

The variations of biphenyl and phenyl benzoate yields with oxygen concentration are shown in Table I.[7] Phenyl benzoate is formed at the expense of biphenyl as is required by the proposed mechanism.[10] Benzoic acid yields remain relatively constant at 40 ± 10%. In this respect our observations differ significantly from those in ref 1, where the data indicate that formation of phenyl benzoate is at the expense of benzoic acid.

The photolysis of benzoyl peroxide in the presence of oxygen was also carried out in ~1:1 mixtures of benzene-d_0 and benzene-d_6. The deuterium distributions of phenyl benzoate and biphenyl, determined by mass spectrometry, are shown in Table II. Phenyl benzoate formation shows large apparent deuterium isotope effects at both oxygen concentrations, in contrast with the much smaller isotope effect for biphenyl formation under the same conditions.

The addition of phenyl radicals to benzene, step 4, has been shown not to be freely reversible.[13,14] Accordingly, step 4 is the rate-determining step for biphenyl formation, and the d_0/d_5 ratio in the product should reflect the deuterium isotope effect in k_4 and should be independent of the oxygen concentration, eq 1. The data in Table II give $k_4^{\mathrm{H}}/k_4^{\mathrm{D}}$ values at

$$\frac{k_4^{\mathrm{D}}}{k_4^{\mathrm{H}}} = \frac{[\mathrm{C_6H_6}]}{[\mathrm{C_6D_6}]}\left(\frac{d_5}{d_0} - \frac{[\mathrm{C_6HD_5}]}{6[\mathrm{C_6H_6}]}\right) \tag{1}$$

30° of 1.15 and 1.27 at the low and high oxygen concentration, respectively. The two values are within experimental error of each other and can be compared with $k_4^{\mathrm{H}}/k_4^{\mathrm{D}} = 1.06$ obtained at a higher temperature from the thermal decomposition of phenylazotriphenylmethane in benzene.[14] Were step 4 partially reversible under our reaction conditions, eq 1 would have given a lower apparent $k_4^{\mathrm{H}}/k_4^{\mathrm{D}}$ value at the higher oxygen concentration. Since this is not the case, our observations support the notion that step 4 is not reversible.[13,14] Since step 4 involves $sp^2 \rightarrow sp^3$ rehybridization, an inverse secondary isotope effect had been expected as has been observed for the addition of methyl radicals to styrene[15] and the free-radical polymerization of styrene.[16,17] The normal isotope effect suggests a weakening of the C–H bonds at the other positions of the benzene ring in the transition state.[18,19]

With toluene, *p*-xylene, or chlorobenzene as solvents the yield of phenyl benzoate from the photochemical decomposition of benzoyl peroxide in the presence of oxygen is 11%.[1] This observation as well as the formation of a comparable amount of phenyl benzoate in benzene in the absence of oxygen, Table I and ref 1, can be accounted for if a significant fraction of excited peroxide molecules decompose by two-bond cleavage followed by cage recombination of phenyl and benzoyloxy radicals, eq 2 and 3.[1] The deuterium

$$\mathrm{PhCO_2O_2CPh} \xrightarrow[\mathrm{ArH}]{h\nu} \overline{\mathrm{PhCO_2\cdot} + \mathrm{Ph\cdot}} + \mathrm{CO_2} \tag{2}$$

$$\overline{\mathrm{PhCO_2\cdot} + \mathrm{Ph\cdot}} \longrightarrow \mathrm{PhCO_2Ph} \tag{3}$$

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(7) Irradiations were carried out using 450- and 550-W high-pressure Hanovia mercury lamps and a Pyrex immersion probe. Reaction vessels and probe were immersed in a water bath thermostated at 30°. Reaction vessels were provided with fritted disk gas inlets and reflux condensers. The oxygen concentration was varied by using nitrogen–oxygen mixtures and rapid gas flow rates to ensure saturation (30 ml/min).[8] Work-up procedures have been described.[2]

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distributions for phenyl benzoate reported in Table II include d_0 phenyl benzoate from the cage reaction. Assuming that the cage reaction contributes an absolute yield of 11% to the observed phenyl benzoate yields, Table II, the calculated d_0/d_5 ratios for phenyl benzoate produced from free benzoyloxy radicals are 3.0_0 and 2.2_8 for 1.5×10^{-3} and 7.2×10^{-3} M oxygen, respectively.[20] The magnitude of these ratios can only be consistent with considerable C–H bond breaking in the rate-determining step for phenyl benzoate formation. The mechanism in Scheme I yields eq 4,

$$\frac{k_2^{\mathrm{H}}}{k_2^{\mathrm{D}}}\frac{K_1^{\mathrm{H}}}{K_1^{\mathrm{D}}} = \frac{[\mathrm{C_6D_6}]}{[\mathrm{C_6H_6}]}\left(\frac{1 + \dfrac{k_2^{\mathrm{H}}}{k_{-1}^{\mathrm{H}}}[\mathrm{O_2}]}{1 + \dfrac{k_2^{\mathrm{D}}}{k_{-1}^{\mathrm{D}}}[\mathrm{O_2}]}\right)\left(\frac{d_5}{d_0} - \frac{[\mathrm{C_6HD_5}]}{6[\mathrm{C_6H_6}]}\right)^{-1} \tag{4}$$

which relates the d_5/d_0 ratio of the phenyl benzoate formed outside the cage with the oxygen concentration, the solvent composition, and the rate constants.

Equation 4 can be used to solve for $(k_2^{\mathrm{H}}K_1^{\mathrm{H}}/k_2^{\mathrm{D}}K_1^{\mathrm{D}})$ by assuming different values of $k_1^{\mathrm{H}}/k_1^{\mathrm{D}}$. A value of $(k_2^{\mathrm{H}}K_1^{\mathrm{H}}/k_2^{\mathrm{D}}K_1^{\mathrm{D}}] = 3.1$ at 30° is obtained, which is insensitive to small deviation of $k_1^{\mathrm{H}}/k_1^{\mathrm{D}}$ from unity. Since $K_1^{\mathrm{H}}/K_1^{\mathrm{D}}$ is not expected to be significantly different from unity, the ratio reflects mainly the normal isotope effect in the rate constant for the abstraction step, k_2.[21]

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[20] For example, in the case of 7.2×10^{-3} M oxygen 11% of the phenyl benzoate is produced by the cage process and the remaining 35% by the noncage process. If x is the fraction of phenyl benzoate-d_0 produced outside the cage, then $(d_0/d_5)_{\mathrm{obsd}} = (0.11 + 0.35x)/0.35(1 - x)$, and using the observed d_0/d_5 ratio in Table II, $x = 0.69_5$. It follows that in this case the d_0/d_5 ratio of the phenyl benzoate produced outside the cage is 2.2_8.

[21] The much smaller deuterium isotope effect observed for an intramolecular attack of the *o*-phenylbenzoyloxy radical to give the corresponding lactone suggests that cyclization is rate determining in that case.[22]

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Jack Saltiel,* Howell C. Curtis[23]
Department of Chemistry, The Florida State University
Tallahassee, Florida 32306

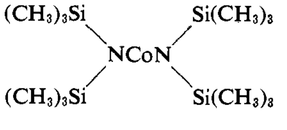
Received January 4, 1971

Bis(hexamethyldisilylamino)cobalt(II), a Two-Coordinated Cobalt Compound

Sir:

Recently tris(hexamethyldisilylamino)iron(III) was shown to be a monomer giving rise to the unusual coordination number of three for the iron atom.[1]

As part of a continuing study of low-coordination metal–nitrogen compounds we have investigated bis(hexamethyldisilylamino)cobalt(II) which had previously been prepared by Wannagat and Bürger,[2] but not completely characterized.



The high volatility (bp 101° (0.6 mm)), the high solubility in nonpolar solvents, and the reactivity to water and oxygen suggested that this compound was possibly monomeric with cobalt exhibiting the unusual coordination number of two.

We have determined its molecular weight both in cyclohexane (cryoscopically) and mass spectroscopically. It is monomeric in solution and gave a parent ion at m/e 379 which is consistent with a monomer in the gas phase.

The uv and visible spectra were obtained in dilute hexane solution, in the crystalline state, and in the liquid phase. Attempts are being made to obtain a gas-phase spectrum. All the spectra were very similar indicating that the coordination number probably remains the same in each state. The results are shown in Table I and are compared with those obtained for gaseous cobalt chloride. The uv and visible spectra of gaseous cobalt chloride have been interpreted assuming $D_{\infty h}$ symmetry in a ligand field formalism.[3,4]

Table I. Ultraviolet and Visible Spectra (Absorption Maxima cm^{-1})

Dilute soln	Solid	Liquid	$\mathrm{CoCl_2}$ (gas)	Assignment for $\mathrm{CoCl_2}$
		31,300		
24,400	20,600	24,400	19,000	$^4\Sigma_g^- \rightarrow {}^4\pi_g(\mathrm{P})$
17,100	17,200	17,000	14,500	$^4\Sigma_g^- \rightarrow {}^4\Sigma_g^-(\mathrm{P})$
14,600	14,700	14,700	10,300	$^4\Sigma_g^- \rightarrow {}^4\Delta_g(\mathrm{F})$
6,500			4,000	$^4\Sigma_g^- \rightarrow {}^4\pi_g(\mathrm{F})$

Comparing the ligand field strengths in vanadium(IV) compounds has shown that the ligand field strength of the $\mathrm{NR_2}$ group is much larger than that of Cl.[5] Assuming this also to be the case for cobalt, then the assignments shown in Table I seem reasonable on the basis of a linear NCoN system.

The corresponding compounds of zinc, cadmium, and mercury have been shown (by a normal coordinate analysis of the liquid ir and Raman spectra) to have linear NMN systems.[6] The ir spectrum of the carbon tetrachloride solution of the cobalt silylamide is shown in Table II and compared with the spectrum of the

Table II. Ir Spectra[a]

Co, cm^{-1}	Zn	Assignments
1258 vs	1268 s (sh)	$\delta_s(\mathrm{CH_3})$
1247 vs	1257 vs	$\delta_s(\mathrm{CH_3})$
995–985 vs	985 vs	$\nu_{as}(\mathrm{NSi_2})$
840–830 vs	835 vs	$\rho(\mathrm{CH_3})$
672 s	674 s	$\nu(\mathrm{SiC_3})$
615 m	612 m	$\nu(\mathrm{SiC_3})$
362 s	436 s	$\nu_{as}(\mathrm{MN_2})$

[a] vs = very strong, s = strong, m = medium, ν_s = symmetric bending, ν_{as} = asymmetric stretching, ρ = rocking mode, sh = shoulder, δ_s = symmetric deformation.

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