

A Mechanistic Study of the Copper(II)-Catalyzed Oxidation of Fluorene with Molecular Oxygen

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Salts of Cu(II), containing a benzoate and a methoxide ion, in the presence of aliphatic amines, catalyze the reaction of fluorene with oxygen in pyridine-methanol solutions at 25°. Fluorenone is the major product and small amounts of bifluorenyl are formed. Kinetic studies indicate that removal of the 9 proton is the rate-determining step. With excess triethylenetetramine present spectral evidence indicates that Cu(I) complexes are not formed during catalysis and kinetic studies show that the Cu(II) catalyst system is 500 times as active as the corresponding catalysis by sodium methoxide. Oxidations in CH₃OD-pyridine solvent suggest that this marked catalysis by copper is due to an increase of greater than 10⁴ in the ratio of the rate constants for reaction of fluorenyl anion by electron and proton transfer.

The reactions of a variety of organic molecules with molecular oxygen are catalyzed by copper salts and amines. Many of the reactions reported involve the breaking of an X-H bond where X is most commonly O, C, or N. Thus molecules such as phenols,¹ *p*-nitrotoluene,² acetylenes,³ α,β -unsaturated ketones,⁴ nitriles,⁵ and aromatic amines⁶ are susceptible to catalysis. Usually the major products result from coupling. However, α,β -unsaturated ketones yield oxygenated products.⁷ With phenols, acetylenes, and amines it is generally observed that Cu(I) salts are more effective catalysts than Cu(II) salts. It has been shown that the autoxidation of Cu(I) salts in hydroxylic solvents forms amine complexes of Cu(II) containing a basic ligand such as OH⁻ or CH₃O⁻^{1b,8,9} and the basicity of these ligands has been assumed to be responsible for the enhanced catalytic activity of the Cu(I) salts. The catalytic activity of added methoxide ions has been demonstrated in Cu(II)-catalyzed autoxidations of unsaturated ketones.¹⁰ In some cases it has been shown that a Cu(II) species acts directly as an oxidizing agent.^{5,11} Only a limited amount of information is available on the relationship between the structures of the complexes, reactivity, and properties such as base strength, redox potential, and ability to coordinate with intermediates formed during oxidation.^{1b,9,11}

In the course of searching for a representative reaction to study, a marked acceleration in rate was observed for the oxidation of the hydrocarbon fluorene when catalytic amounts of cuprous chloride or carboxylate salts and aliphatic polyamines were present in pyridine-methanol solutions at 25°. Since no report of the large catalytic effect in this system appeared to have been made, a detailed study was carried out. In this paper results are presented which allow

some conclusions on the general mechanism and in particular on the relationship of catalyst structures, anionic species, and catalytic reactivity. Some general conclusions on related types of catalysis are drawn.

Results

It was first established that the only significant reaction of cuprous chloride and carboxylate salts in pyridine-methanol solutions under oxygen pressure at 25° is the formation of mixed salts of Cu(II) containing a methoxide ion and the corresponding anion of the cuprous salt in agreement with a previous report.⁹

These Cu(II) salts then were synthesized and it was observed that the catalytic rates with the cuprous salts are the same as with the cupric except that a small amount of oxygen is absorbed initially with cuprous salts to form cupric compounds, causing difficulties in kinetic measurements. Therefore, for experimental convenience the detailed mechanism studies were carried out with the Cu(II) salts. For better solubility, salts containing a benzoate ion were chosen for most of the experiments.

In all these reactions the rates of exchange of the ligands at the copper centers are many times greater than the overall reaction rates.¹² Therefore, the order of addition of the reactants will not affect the observed results. Except where specified, the solvent is a mixture of five volumes of pyridine to one volume of methanol. The temperature in all runs is 25.0°. The rates of oxygen uptake could not be described by any simple kinetic expression over the complete course of the reactions. A first-order kinetic plot was made for a typical run such as run 60B in Table I and was linear over the initial 40-60% of the reaction. The value of the rate constant is $8.5 \times 10^{-4} \text{ sec}^{-1}$. During the later stages retardation of the rate appeared and first-order kinetics were no longer obeyed. The retardation is not due to appearance of the major reaction products, water and fluorenone, since addition of each of them, in amounts formed during reaction, caused no change in initial rates. To avoid the complexities of the later stages of reaction all rates were measured at 1% conversion of the fluorene.

Ligand Effects.—Significant reaction only occurs when the molar ratio of available amine groups to copper is greater than three, as shown by the plots in Figure 1, where ethylenediamine (en), diethylenetriamine

(1) (a) G. F. Endres, A. S. Hay, and J. W. Eustance, *J. Org. Chem.*, **28**, 1300 (1963); (b) E. Ochiai, *Tetrahedron*, **20**, 1831 (1964); (c) Y. Ogata and T. Morimoto, *ibid.*, **21**, 2791 (1965).

(2) H. A. Stansbury and W. R. Proops, *J. Org. Chem.*, **26**, 4162 (1961).

(3) H. A. Stansbury and W. R. Proops, *ibid.*, **27**, 320 (1962); A. S. Hay, *ibid.*, **27**, 3320 (1962).

(4) H. C. Volger and W. Brackman, *Recl. Trav. Chim. Pays-Bas*, **84**, 579, 1203 (1965).

(5) M. S. Karasch and G. Sosnovsky, *Tetrahedron*, **3**, 97 (1958).

(6) K. Kinoshita, *Bull. Chem. Soc. Jap.*, **32**, 777, 780 (1959).

(7) Coupling is reported in the absence of O₂; see ref 8.

(8) H. C. Volger and W. Brackman, *Recl. Trav. Chim. Pays-Bas*, **84**, 1233 (1965).

(9) H. Finkbeiner, A. S. Hay, H. S. Blanchard, and G. F. Endres, *J. Org. Chem.*, **31**, 549 (1966).

(10) H. C. Volger and W. Brackman, *Recl. Trav. Chim. Pays-Bas*, **86**, 244 (1967).

(11) H. C. Volger and W. Brackman, *ibid.*, **85**, 818 (1966).

(12) R. G. Pearson and R. D. Lanier, *J. Amer. Chem. Soc.*, **86**, 765 (1964).

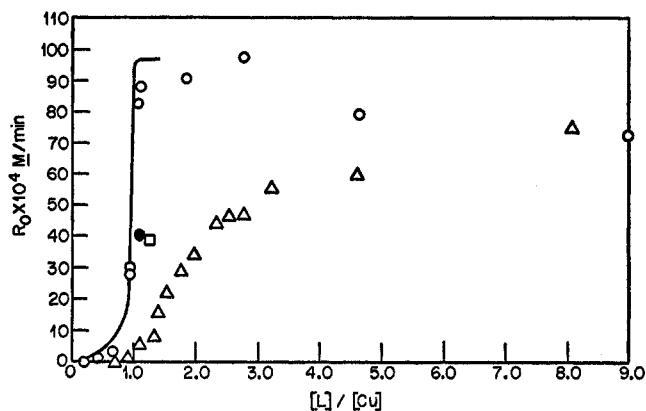


Figure 1.—Initial rate of oxygen uptake vs. $[\text{ligand}]/[\text{Cu}(\text{Obz})(\text{OCH}_3)]$, where $[\text{Cu}(\text{Obz})(\text{OCH}_3)] = 2.50 \times 10^{-3} M$: O, trien, $[\text{FlH}_2] = 0.200 M$; Δ , en, $[\text{FlH}_2] = 0.100 M$; \square , dien, $[\text{FlH}_2] = 0.100 M$; \bullet , tetraen, $[\text{FlH}_2] = 0.100 M$. The solid line is a plot of the calculated concentration of free (trien) $\text{Cu}(\text{Obz})(\text{OCH}_3)$ species.

TABLE I
EFFECTS OF LIGANDS AND METAL ON INITIAL OXIDATION RATES (R_0) OF 0.100 M FLUORENE IN 5:1 PYRIDINE- CH_3OH AT 25.0° AND 950 TORR OF O_2 WITH 0.0025 M CATALYST

Run	Catalyst	Amine	Amine/ catalyst	R_0 , M/min $\times 10^4$
60B	$\text{Cu}(\text{Obz})(\text{OCH}_3)$	Trien	2.22	50
65	$\text{Cu}(\text{OCH}_3)_2$	Trien	2.20	$\sim 115^a$
96	$\text{Cu}(\text{Obz})_2$	Trien	2.21	136^b
49B	$\text{Cu}(\text{Obz})\text{OCH}(\text{CH}_3)(\text{CH}_2\text{NH}_2)$	Dien	1.09	18
51A	$\text{Cu}(\text{Obz})\text{OCH}(\text{CH}_3)(\text{CH}_2\text{NH}_2)$	Trien	1.10	33
59B	$\text{Cu}(\text{Obz})(\text{OCH}_3)$	Dien	1.42	36
52B	$\text{Cu}(\text{Cl})(\text{OCH}_3)$	En	2.19	32
	$\text{Cu}(\text{Obz})(\text{OCH}_3)$	En	2.19	41^c
96	NaOCH_3	Trien		0.19^b
9	NaOCH_3			0.51^d

^a Catalyst was slow to dissolve; so the rate was taken after several per cent reaction. ^b Solution contains added NaOCH_3 (0.0107 M) and is 0.050 M in fluorene. Before the $\text{Cu}(\text{Obz})_2$ was added $R_0 = 0.2 \times 10^{-4}$. After addition of the $\text{Cu}(\text{Obz})_2$ $R_0 = 136 \times 10^{-4}$. ^c Interpolated from plot in Figure 1. ^d Solution contains added NaOCH_3 (0.0150 M). After 10 min reaction $\text{Cu}(\text{Obz})_2$ ($2.5 \times 10^{-3} M$) was added but a precipitate formed and the rate dropped to 0.28×10^{-4} .

(dien), and triethylenetetramine (trien) were used as ligands. Negligible rates are observed with N,N,N',N' -tetramethylethylenediamine and bipyridyl even in large excesses.

There is no observable oxygen uptake unless methoxide ions are present in the reaction mixture. Runs 60B, 65, and 96 (Table I) show the effects of adding methoxide in different ways. In runs 49B and 51A the alkoxide group was included as 1-amino-2-propoxide ion, a bidentate type ligand.

There appears to be no specific effect of the benzoate group. If the benzoate ion is replaced by chloride ion (compare R_0 in run 52B with the comparable value interpolated from Figure 1), R_0 decreases by about 22%, and, if benzoate is replaced by methoxide (compare run 60B with run 65), the rate approximately doubles. The benzoate group was the preferred ligand in these reactions because of the solubility it imparts to the copper compound in organic solvents compared with chloride and other inorganic ions.

Effect of Fluorene Concentration.—The initial rates of oxygen uptake depend on the fluorene concentration in a first-order manner (Figure 2). The blank reaction

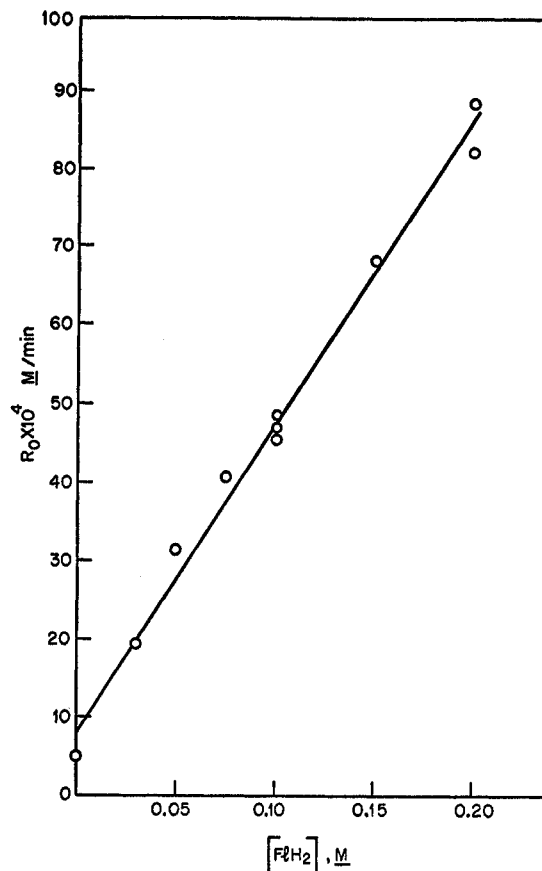


Figure 2.—Initial rate of O_2 uptake vs. concentration of fluorene $[\text{Cu}(\text{Obz})(\text{OCH}_3)] = 2.5 \times 10^{-3} M$, $[\text{trien}] = 2.7 \times 10^{-3} M$, $P_{\text{O}_2} = 950$ Torr.

observed at zero fluorene (Figure 1) leads to a total O_2 absorption of less than 1.5 mmol per mmole of catalyst. Possibly the amine ligand groups are oxidized, causing termination of catalytic activity. From the slope the value of the pseudo-first-order rate constant is $6.6 \times 10^{-4} \text{ sec}^{-1}$. On the basis that the reaction is also first order in catalyst (see below), the second-order rate constant has a value of $0.26 M^{-1} \text{ sec}^{-1}$.

Effect of Catalyst Concentration.—Between 2.5×10^{-3} and $7.0 \times 10^{-3} M$ catalyst in 0.100 M fluorene solutions the oxygen uptake is first order in catalyst and between 0 and $2.5 \times 10^{-3} M$ the rate falls off slightly (Figure 3). The low concentration points probably fall off because the total concentration of amine is insufficient to maintain as high a percentage of the copper in the complexed form as with the higher concentration runs. From the slope the pseudo-first-order rate constant is $3.1 \times 10^{-2} \text{ sec}^{-1}$. The bimolecular rate constant is $(3.1 \times 10^{-2})/0.100 = 0.31 M^{-1} \text{ sec}^{-1}$, in good agreement with the values obtained from hydrocarbon variation, 0.26, and from the value calculated from the first-order kinetic plot of the initial 50% of reaction for run 60B, 0.34.

Effect of Oxygen Pressure.—The rate of oxygen uptake is essentially independent of O_2 pressure in the range 200–1950 Torr (Figure 4).

Effect of Solvent.—When the reaction components were homogeneously mixed in $\text{CH}_3\text{OH}-\text{C}_6\text{H}_6$ (1.5:1.0, v/v) and $\text{CH}_3\text{OH}-\text{CCl}_4$ (1.5:1.0, v/v) mixtures, no O_2 uptake occurred. However, when neat pyridine was used as solvent, the reaction rates were normal. When

TABLE II
OXYGEN PRESSURE DEPENDENCE OF THE PRODUCTS OF THE OXIDATION OF 0.100 M FLUORENE WITH
 $5.0 \times 10^{-3} M$ Cu(OBz)(OCH₃) AND $1.09 \times 10^{-2} M$ TRIEN^a

Run	P _{O₂}	ΔF _{FIH₂}	% Reaction	F=O	(FIH) ₂	F=O/(FIH) ₂	Unaccounted fluorene
84	1950	1.07	54	1.09	5.5×10^{-3}	2.0×10^2	
88	1950	0.99	50	0.98	4.9×10^{-3}	2.0×10^2	
85	200	0.94	47	0.76	0.039	20	0.10
92	200	1.00	50	0.90	0.046	20	0.01
87	44	0.48	24	0.029	0.035	0.83	0.38
93 ^b	0				6.1×10^{-3}		

^a Product yields are given in millimoles. ^b The catalyst and trien concentrations were double those of the other runs and the reaction was run for 10 min. The other reactions in the table were run for 5–6 min.

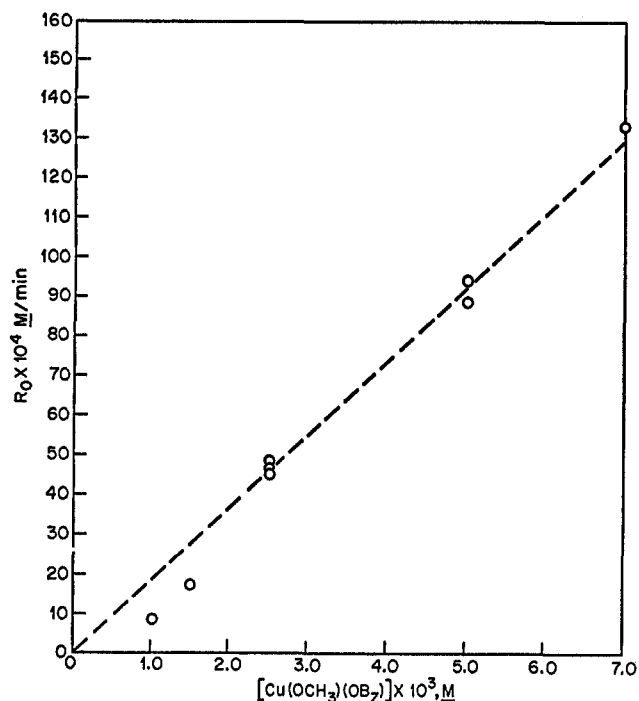


Figure 3.—Initial rate of O₂ uptake vs. [Cu(OBz)(OCH₃)]/[trien]/[Cu] = 1.1, P_{O₂} = 950 Torr, [FIH₂] = 0.100 M.

0.2 M benzene was added to a normal reaction mixture, no change in initial rate occurred.

Isotope Effect.—Duplicate runs of 0.100 M solutions of 9-dideuteriofluorene (96% deuterated in the 9 position) with $2.50 \times 10^{-3} M$ Cu(OBz)(OCH₃), $2.78 \times 10^{-3} M$ trien, and 950 Torr of O₂ gave initial rates of 6.5 and $7.0 \times 10^{-4} M \text{ min}^{-1}$. Duplicate runs under identical conditions with fluorene gave rates of 45 and $47 \times 10^{-4} M \text{ min}^{-1}$. On the basis of the 96% deuteration of the deuterated sample the average isotope effect, $R_0(\text{H})/R_0(\text{D})$, is 9.0.

Products.—The relative rates of product formation are oxygen pressure dependent (Table II). At the highest pressure fluorenone and 9,9'-bifluorenyl account for all the fluorene consumed within experimental error. At 200 Torr the material balance is still good but at 44 Torr the fate of much of the consumed fluorene is unknown. The unknown products are not 9-fluorenol, bifluorylidene, or 9-methoxyfluorene. In a run under N₂ (run 93, Table II) after 10 min 6.1×10^{-3} mmol of (FIH)₂ were recovered. Some oxygen was introduced into the final reaction mixture during manipulation. Hydrogen peroxide, a possible reaction product, cannot be observed because of its instability under the reaction

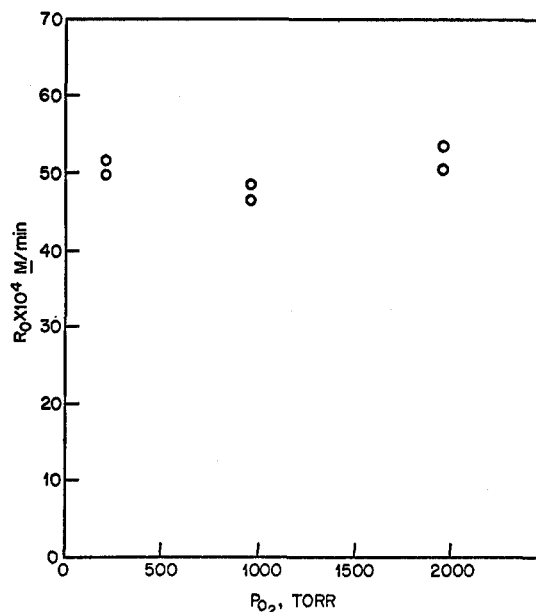


Figure 4.—Dependence of initial rate of O₂ uptake on O₂ pressure for 0.100 M fluorene, $2.50 \times 10^{-3} M$ Cu(OBz)(OCH₃), and $2.78 \times 10^{-3} M$ trien.

conditions. When a sample is added to a reaction mixture, gas is vigorously evolved.

Exchange Reactions.—The 9 protons in fluorene are exchanged for deuterium atoms in oxygen-free pyridine-CH₃OD solutions containing NaOCH₃ or Cu(OBz)(OCH₃) with excess trien. The results of nmr analysis of the recovered and recrystallized fluorene are shown in Table III. The analyses are accurate to within about 5%.

A 0.100 M solution of fluorene was oxidized at 950 Torr of O₂ to 50% conversion of the fluorene with $2.5 \times 10^{-3} M$ Cu(OBz)(OCH₃) and $5.18 \times 10^{-3} M$ trien using pyridine-CH₃OD (5:1, v/v) as the solvent. The unreacted fluorene was recovered and purified by preparative gas chromatography. Mass spectral analysis showed that 3.2% of the fluorene contained one deuterium atom. A similar run was done at 150 Torr of O₂. The mass spectral analysis showed that 2.3% of the recovered fluorene was monodeuterated at about 50% conversion. A control experiment without copper (run 18, Table III) showed 2.9% exchange for the same reaction time.

Spectra.—The visible spectra of solutions containing combinations of Cu(OBz)(OCH₃), trien, and fluorene in the presence and absence of O₂ are shown in Figure 5. The esr spectra at 77°K and room temperature of

TABLE III
DEUTERIUM EXCHANGE OF THE 9 PROTONS OF 0.200 M FLUORENE IN O₂-FREE PYRIDINE-CH₃OD (5:1, v/v)
SOLUTION^a AT 25.0°. ANALYSIS BY NMR AND MASS SPECTROMETER

Run	[Cu(OBz)(OCH ₃)]	[trien]	[NaOCH ₃]	Time, min	% Exchange	Analysis
121			1.14 × 10 ⁻²	5.0	67	Nmr
122	1.01 × 10 ⁻²	1.07 × 10 ⁻²		5.0	39	Nmr
120		1.07 × 10 ⁻²		15.0	<5-7	Nmr
18		5.2 × 10 ⁻³		10.0	2.9	Mass spectrum

^a All concentrations are in moles/liter.

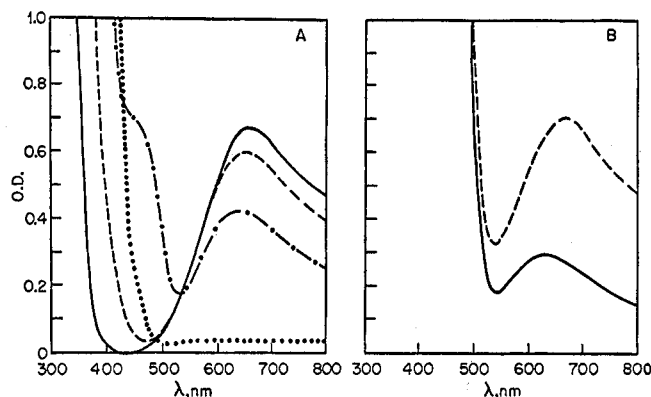


Figure 5.—Visible spectra of O₂-free and O₂-saturated Cu-catalyst solutions. A: —, no fluorene, [Cu(OBz)(OCH₃)] = 5.0 × 10⁻³ M, [trien] = 2.1 × 10⁻² M; ---, [FIH₂] = 0.10 M, [Cu(OBz)(OCH₃)] = 5.0 × 10⁻³ M, [trien] = 2.1 × 10⁻² M, no O₂, 3 min after mixing; - · - · -, same as --- but 2 hr after mixing; · · · · ·, [Cu(I)OBz] = 2.5 × 10⁻³ M, [trien] = 1.5 × 10⁻² M, no O₂. B: —, [FIH₂] = 0.10 M, [Cu(OBz)(OCH₃)] = 5.0 × 10⁻³ M, [trien] = 2.1 × 10⁻² M, no O₂, 2 days after mixing; - · - · -, same as — but solution saturated with O₂.

solutions of Cu(OBz)(OCH₃) and trien with and without fluorene and O₂ are shown in Figure 6. At 2°K the values of the *g* and *A* parameters are *g*₁₁ = 2.21, *g*_⊥ = 2.06, *A*₁₁ = 554 MHz, and *A*_⊥ ~ 0.

Discussion

Kinetics.—Reactions 1-11 are proposed to explain the experimental observations. The reactive complex of Cu(II) must have three or four amine ligands, as concluded from the plots of Figure 1. Most of the kinetic data were obtained using trien as the amine ligand, so in the discussion below the active complex is [(trien)Cu(II)]²⁺ which is represented by LCu(II) where L ≡ trien. Although free ions are written below, it is understood that the predominant ionic species are probably ion pairs.

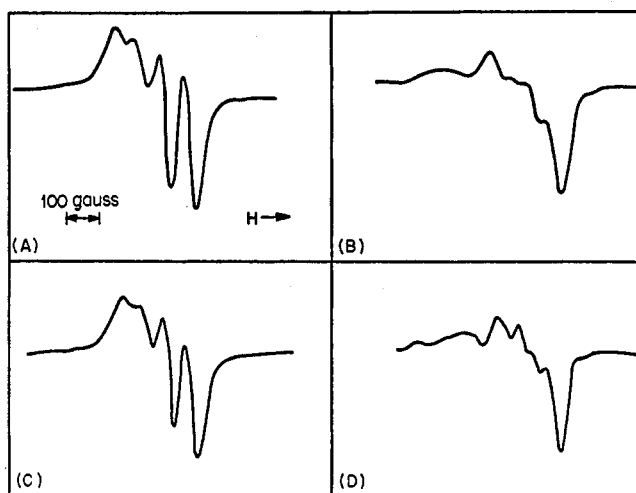
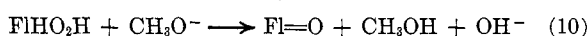
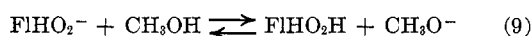
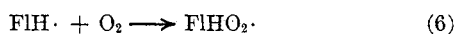
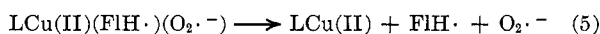
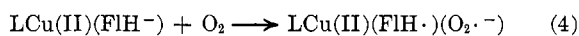
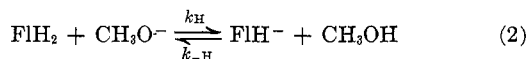
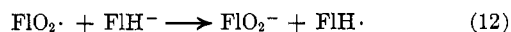


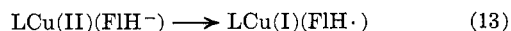
Figure 6.—The esr spectra of pyridine-methanol solutions containing 5.0 × 10⁻³ M Cu(OBz)(OCH₃) and 2.3 × 10⁻² M trien. A and B are O₂-free solutions containing 0.10 M fluorene. Spectra of A and B were taken 15 min after mixing at room temperature. A and C are at ambient temperature; B and D are at 77°K.

The general scheme is based on those proposed earlier by Russell and coworkers^{13,14} for the base-catalyzed oxidation of fluorene. It appears that the present data are best explained on the basis that the effect of the copper salt is to supply a base (the methoxide ion) and a Cu(II) species which acts as an electron transfer catalyst. These points now will be discussed in detail.

A fluorenyl anion is produced in the forward step of reaction 2. The required methoxide ion can be associated either with a copper ion (see Figure 3 and run 65, Table I) or an inert sodium ion (see run 96, Table I). The fluorenyl anion, after complexing with LCu(II), can react by electron transfer with an oxygen molecule (*via* reactions 3 and 4), or by proton transfer from solvent (reverse step of reaction 2). Electron transfer to a fluorenyl peroxy radical (reaction 12) is a possible



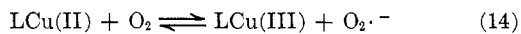
reaction in this system. However, this reaction has been shown to be negligible in the base-catalyzed autoxidation of fluorene in the presence of *m*-trifluoromethylnitrobenzene, a very active one-electron oxidizing agent.¹⁴ In this case¹⁴ the kinetics were zero order in catalyst and oxygen. In analogy with these observations reaction 12 is assumed to be negligible in the present discussion. Oxidation of the fluorenyl anion by direct electron transfer to Cu(II) (reaction 13) is excluded by spectral evidence (see below). The



(13) G. A. Russell, *et al.*, *Advan. Chem. Ser.*, **51**, 122 (1965).

(14) G. A. Russell, *et al.*, *ibid.*, **75**, 174 (1968).

formation of low concentrations of a reactive, transient Cu(III) species which can act as an oxidizing agent for FIH⁻ is consistent with the observed data (reactions 14 and 15). However, since there is no direct evidence



for Cu(III) at present (see below), reactions 3 or 4 are preferred. The results (see below) of deuterium exchange experiments indicate that protonation is much slower than electron transfer; thus in terms of the rate scheme

$$r_{\text{ox}} \ll k_{-\text{H}}[\text{CH}_3\text{OH}]$$

where

$$r_{\text{ox}} = \frac{k_2 k_4 [\text{LCu(II)}] [\text{O}_2]}{(k_{-3} + k_4)}$$

The quantity r_{ox} represents the total pseudo-first-order rate constant for the oxidation of the fluorenyl anion. With the above inequality the complete steady state rate expression reduces to

$$\frac{-d[\text{FIH}_2]}{dt} = k_{\text{H}}[\text{FIH}_2][\text{CH}_3\text{O}^-] \quad (16)$$

and proton loss becomes rate determining. Since fluorenone is the major product observed, $-d[\text{O}_2]/dt \equiv R_0 \cong -d[\text{FIH}_2]/dt$ (one fluorene is consumed per oxygen), and eq 16 then agrees with the observed kinetics (Figures 2, 3, and 4). The experiments with added sodium methoxide (see above) imply that the observed first-order dependence on total Cu(OBz)-(OCH₃) added (Figure 3) is due to the methoxide ion released in reaction 1. It follows then that the overall rate is independent of [LCu(II)] over the concentration range studied ($>1 \times 10^{-3} M$) as required by the theoretical rate expression.

From the plots of Figures 2 and 3, values of 0.26 and 0.31 $M^{-1} \text{sec}^{-1}$ are obtained respectively for k_{H} . In the absence of O₂, exchange of the 9 protons with deuterium atoms from CH₃OD occurs at similar rates for the copper catalyst system and sodium methoxide (Table III). On the basis that exchange is first order each in hydrocarbon and base,^{14,15} the value of k_{H} calculated from run 122, Table III, is 0.2 $M^{-1} \text{sec}^{-1}$, in reasonable agreement with the above values. The observed isotope effect of $k_{\text{H}}/k_{\text{D}} \sim 9.0$ is in reasonable agreement with the value of 10 measured by Russell, *et al.*, for fluorene in *tert*-butyl alcohol using potassium *tert*-butoxide.¹⁴

The assumption that capture of the fluorenyl anion by oxidizing agent is faster than capture by proton is valid, since no more than 3% deuterium exchange is found at the 9 position of unreacted fluorene remaining in a 50% conversion oxidation at 950 and at 150 Torr of oxygen. It follows then that at 950 and 150 Torr

$$r_{\text{ox}}/r_{-\text{H}} > 97/3 \sim 32$$

where r_{ox} is as defined previously and

$$r_{-\text{H}} = k_{-\text{H}}[\text{CH}_3\text{OH}]$$

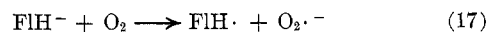
Quantitative determination of the ratio is limited by the blank reaction exchange (Table III).

(15) D. Bethell and R. J. E. Talbot, *J. Chem. Soc. B*, 638 (1968).

The internal electron transfer step, reaction 13, can be ruled out as an important path in the oxidation by visible and esr spectral measurements. The broad band at 650 nm is characteristic of the d-d transitions in Cu(II) complexes and is absent in Cu(I) complexes (Figure 5).¹⁶ Very similar bands have been observed in [(en)₂Cu(II)]²⁺ complexes.¹⁷ The rate of disappearance of this band in an oxygen-free reaction mixture (Figure 5) is slower than both exchange under comparable conditions and oxidation in the presence of oxygen. During the initial 2-hr life of a freshly mixed, oxygen-free solution containing 0.100 M fluorene, $4.92 \times 10^{-3} M$ Cu(OCH₃)(OBz), and $2.31 \times 10^{-2} M$ trien at 24.3° the intensity of the 650-nm band only decreased by 37%. The rate of decrease does not follow any simple first- or second-order kinetic dependence but the average rate over this period is roughly $1.5 \times 10^{-5} M \text{min}^{-1}$ or about 400-fold slower than the rate of oxidation. The shoulder which slowly appears between 450 and 480 nm may be due to $\Delta^{9,9'}$ -bifluorenyl, which has a reported maximum (CCl₄) at 460 nm (log ϵ 4.1).¹⁸ An absorbance of unity would correspond to a concentration of $8 \times 10^{-5} M$. The esr signal observed in this same solution 15 min after mixing at room temperature (Figure 6) has roughly the same intensity and appearance as a similar solution without fluorene. Since Cu(I) is diamagnetic no significant change in oxidation state could have occurred.

The observed similarities of the visible and esr spectra of oxygenated and degassed solutions of the copper complexes suggests that Cu(III) species, if formed (perhaps by reactions 14 or 15), are present in small amounts. The solubility of oxygen in the solvent system was measured and found to be the same within a few per cent whether or not copper was present (in concentrations up to several times the solubility of oxygen), in agreement with the above conclusion.

Comparison of Sodium and Copper.—It is of interest to compare catalysis with sodium methoxide to catalysis by Cu(OCH₃)(OBz). The overall rates of oxygen uptake can be compared by calculating the rates in runs 96 and 9 (Table I) for 0.200 M fluorene and $2.5 \times 10^{-3} M$ NaOCH₃ on the basis of the known first-order dependence of rate on each of these reactants.^{14,15} On this basis the average value of $R_0(\text{Na})$ is $0.20 \times 10^{-4} M \text{min}^{-1}$ at 950 Torr of O₂. Comparing this to the maximum rate at 950 Torr of O₂ with the (trien)Cu(II) complex in Figure 1 gives a ratio $R_0(\text{Cu(II)})/R_0(\text{Na}) = 4.9 \times 10^2$. The base-catalyzed oxidation of fluorene in *tert*-butyl alcohol is known to be approximately first order each in base, oxygen, and hydrocarbon^{14,15} and the known mechanism requires reaction 2 in conjunction with reaction 17.



The kinetics thus require $r_{-\text{H}}^{\text{Na}} \gg r_{\text{ox}}^{\text{Na}}$ where $r_{-\text{H}}^{\text{Na}} = k_{-\text{H}}^{\text{Na}} [\text{CH}_3\text{OH}]$ and $r_{\text{ox}}^{\text{Na}} = k_{17}^{\text{Na}} [\text{O}_2]$. Since fluorenone is the only product reported

$$R_0(\text{Na}) = \frac{r_{\text{ox}}^{\text{Na}} k_{\text{H}}^{\text{Na}} [\text{FIH}_2] [\text{CH}_3\text{O}^-]}{r_{17}^{\text{Na}}} \quad (18)$$

(16) The slight absorption of (trien)Cu(I) complex in Figure 5 is due to a small amount of oxidation of the sample during handling.

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From the above rate comparison and dividing equations 16 and 18 we obtain

$$\frac{R_0(\text{Cu})}{R_0(\text{Na})} = \frac{k_{\text{H}}^{\text{Cu}} r_{\text{ox}}^{\text{Na}}}{r_{\text{ox}}^{\text{Cu}} k_{\text{H}}^{\text{Na}}} = 490$$

Since the rates of exchange of the 9 protons catalyzed by NaOCH_3 and the (trien)Cu(II) catalyst are equal within a factor of two (Table III), $k_{\text{H}}^{\text{Cu}} \sim k_{\text{H}}^{\text{Na}}$ and $r_{\text{ox}}^{\text{Na}}/r_{\text{ox}}^{\text{Cu}} \sim 500$. Thus in the sodium methoxide catalyzed autoxidation, protonation of the fluorenyl anion occurs 500 times as often as reaction with oxygen. From the deuterium exchange during oxidation in the Cu(II) system at 950 Torr $r_{\text{ox}}^{\text{Cu}}/r_{\text{ox}}^{\text{Na}} > 32$ and therefore

$$(r_{\text{ox}}^{\text{Cu}}/r_{\text{ox}}^{\text{Na}})/(r_{\text{ox}}^{\text{Na}}/r_{\text{ox}}^{\text{Cu}}) > 1.5 \times 10^4$$

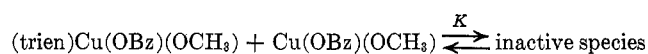
The special catalytic effect of Cu(II) is thus due to the large change in the above anion capture ratios. It follows then that if reaction 12 is indeed negligible the catalytic effect of the copper is specifically due to a decrease in the protonation rate (reaction 2) and/or an increase in the electron transfer rate (reactions 3 and 4) by a total factor of 10^4 or greater.

Catalyst Structures.—Some conclusions can be drawn as to the structures of the copper complexes. The physical evidence suggests that the initial complex has a tetragonal structure with the anions weakly attached to the axial positions or in outer coordination spheres. A pyridine-methanol solution of $\text{Cu}(\text{OBz})(\text{OCH}_3)$ in the presence of excess trien gives the esr spectra shown in Figure 6. The spectrum was also taken at 2°K and the spin parameters calculated from this spectrum are $g_{11} = 2.21$, $g_{\perp} = 2.06$, $A_{11} = 554$ MHz, and $A_{\perp} \sim 0$. These parameters are typical of a symmetrical square planar structure with bonding by four nitrogens¹⁹ and the g tensors are very similar to those found in complexes of the type $(\text{en})_2\text{Cu}(\text{II})\text{X}_2$ where X represents a variety of anions such as chloride and nitrate.¹⁷ It is believed that the anions are very weakly coordinated in the axial positions. Volger and Brackman²⁰ have reported that in methanol-pyridine solutions the species $[(\text{pyridine})_4\text{Cu}(\text{II})]^{2+}$ readily coordinates a methoxide ion as a fifth ligand. However, in the case of the aliphatic amines, the coordination must be very similar to loose ion pairing, since Davis and Patel²¹ have observed a 20-fold rise in the conductance of an aqueous solution of copper malonate when 2 mol of ethylenediamine are added for each mole of copper. On the other hand, methoxide ions are strongly coordinated in the absence of amine ligands and in the case of $\text{Cu}(\text{OCH}_3)_2$ dissolution in pyridine-methanol solvent does not occur readily until polydentate aliphatic amine is added. In the absence of ligands methoxide bridging undoubtedly occurs.

The kinetic evidence is in accord with the above structure. The similar values of k_{H} for NaOCH_3 and (trien)Cu(OBz)(OCH₃) show that the reactivity of the methoxide ion is only slightly affected by the cation and suggest a very weak coordination of the methoxide ion. The fact that pyridine is necessary for oxidation suggests that replacement of the axial ligands by pyridine takes place, and that in the active catalyst complex these ions may exist as outer sphere ligands.

The similar rate with benzoate and chloride ions (Table I) is in accord with this description. The rate of oxidation with the copper catalyst is roughly proportional to the total concentration of methoxide ion added regardless of the cation. Thus, comparing runs 60B, 65, and 96 (Table I) the ratios of total methoxide concentration are 1.0:2.0:4.3 and the respective rates are 1.0:2.3:5.5. However, when the alkoxide ion is connected to an amine group in a bidentate type structure as in the case of the 1-amino-2-propoxide ligand, the oxidation rates are lowered, suggesting that increased coordination of the base group lowers the rate of proton removal. Thus as the amine ligand is changed from dien to trien (runs 49B and 51A, Table I) the rate nearly doubles and the latter rate is nearly that for Cu(OBz)(OCH₃) with dien (run 60B, Table I).

The unusually steep rise in oxidation rate when the ratio of trien concentration to Cu(II) concentration is slightly below unity may be due to additional coordination of the methoxide ion of a reactive catalyst molecule by an uncomplexed Cu(II) species leading to a loss in reactivity of the methoxide ion.



Different values of the equilibrium constant ranging from 10 to 10^5 were assigned, and using the conditions of 0.100 M fluorene and 2.5×10^{-3} M total Cu the equilibrium concentration of (trien)Cu(OBz)(OCH₃) as a function of the trien/Cu ratio was calculated. Assuming that $R_0 = k[(\text{trien})\text{Cu}(\text{OBz})(\text{OCH}_3)]$, k was calculated by equating the observed maximum rate in Figure 1 with the maximum calculated concentration. The calculated plot of R_0 for $K = 10^4$ is shown in Figure 1 and has a fair fit to the observed rate curve.

As regards the structure of the proposed intermediate fluorenyl-copper complex, the fluorenyl anion is probably a weakly bonded axial ligand similar to methoxide. However, additional stabilization is possible by π backbonding from the electron-rich d orbitals of the copper analogous to the proposed bonding of benzene to copper(II) dimethylglyoxime in benzene solutions of the complex.²² It is possible that such a structure could lead to a very facile electron transfer from the axial fluorenyl anion *via* the copper atom to an O₂ molecule located in the other axial position (reaction 4). The fluorenyl anion protonation rate constant may also be lowered for such a structure. Both possibilities are in agreement with the experimental observations.

Product Formation.—The products and their dependence on oxygen pressure (Table II) are qualitatively in accord with the postulated mechanism (reactions 1–11). Since an increase in oxygen pressure will increase reaction 6 but not 11 the yield of fluorenone should increase relative to bifluorenyl as is observed. However, bifluorenyl has not been reported as a product in other catalyzed autoxidations of fluorene in basic media^{18,14} under similar conditions. One possible explanation may be that the fluorenyl radicals (and other intermediates as well) are associated with a Cu(II) species in such a way as to alter the rates of their reactions.

Related Copper-Catalyzed Reactions.—There are other copper-catalyzed reactions in which polyamines

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(22) K. Falk, E. Ivanova, B. Roos, and T. Vanngard, *Inorg. Chem.*, **9**, 556 (1970).

have an accelerating effect on the rate. The autoxidation of 2,6-di-*tert*-butylphenol^{1b} by CuCl in pyridine reaches a maximum rate when the ratio of [en]/[cu] \sim 3. At zero and very high concentrations of ethylenediamine the rate is about 0.125 times as rapid. Roughly the same acceleration is shown by diethylenetriamine when [dien]/[Cu] \sim 1 but at high ratios the rate does not fall off. Triethylenetetramine inhibits the reaction. Thus for maximum reactivity three amine ligands should be coordinated to the copper. It has been reported that the decomposition of H₂O₂ is catalyzed by a bis(2,2-bipyridyl)copper complex, although the 1:1 complex is the most reactive.²³ The present work suggests that in cases where the copper catalyst has three or four aliphatic amine groups strongly coordinated, Cu(II) does not act as an oxidizing agent because of the unfavorable change of the redox potential between Cu(I) and Cu(II) with increasing coordination by polydentate aliphatic amines. This is supported by the observation of Janes and Williams²⁴ that the oxidation potential of the half reaction $L_4Cu(I) = L_4Cu(II) + e$ changes by about 0.66 V when the four ligand sites change from coordination with four pyridines to two ethylenediamines. Thus the bis(ethylenediamine)Cu(II) complex is a substantially weaker oxidizing agent. The Cu(II)-containing enzymes, amine oxidase²⁵ and galactose oxidase,²⁶ appear to function as oxidation catalysts without intervention of a Cu(I) state. However, in these cases the exact nature of the ligands is uncertain.

Experimental Section

Materials.—Standard reagent grade pyridine and methanol were used fresh from well-stoppered bottles without further purification. Deuteriomethanol (99% CH₃OD) was obtained from the Isomet Corp. Ethylenediamine (en), diethylenetriamine (dien), and triethylenetetramine (trien) were distilled from CaH₂ and stored in well-stoppered bottles. Fluorene was recrystallized from hot ethanol to constant melting point (116.5–117.5°).

9-Dideuteriofluorene.—The 9-deuterated fluorene was prepared by repeated exchange in pyridine-CH₃OD mixtures using NaOCH₃. Each exchange was run under N₂ for 2 hr, then quenched by pouring into 1 M HCl solution. The precipitated fluorene was collected by suction filtration, washed several times with water, and dried *in vacuo*. The final sample was 96% deuterated at the 9 position by nmr analysis. After recrystallization from hot aqueous ethanol the melting point was 115.5–116.5°.

Preparation of Copper Compounds. CuCl.—Cuprous chloride was prepared by the method of Walton.²⁷ A white, crystalline powder was obtained.

CuOBz.—Cuprous benzoate was prepared by modifying the method of Cohen and Lewin.²⁸ Benzoic acid (0.11 mol) was dissolved in 200 ml of xylene. Cuprous oxide powder (0.025 mol) was added and the mixture was refluxed under N₂ overnight with a Dean-Stark trap connected to remove water. After reaction, only a trace of red oxide remained and after cooling in ice a white solid formed. The xylene was filtered off under N₂ pressure and the solid was washed with 50 ml of xylene and 25 ml of ether. The solid was then freed of remaining solvent by pumping at 0.2 Torr, leaving 8.5 g of a whitish-gray solid (42% yield). The material discolors in air and must be stored in the dark in a

well-stoppered bottle. *Anal.* Calcd for CuC₇H₅O₂: Cu, 34.4. Found: Cu, 34.1.

Cu(Cl)(OCH₃).—The method of Finkbeiner, *et al.*,¹⁰ was followed, giving a 92% yield. *Anal.* Calcd for CuCH₃OCl: Cu, 48.8. Found: Cu, 48.7.

Cu(OBz)(OCH₃).—The above method for preparation of Cu(Cl)(OCH₃) was used except that CuOBz was substituted for CuCl. *Anal.* Calcd for CuC₈H₅O₃: Cu, 29.5; C, 44.5; H, 3.74. Found: Cu, 29.0; C, 44.2; H, 3.74.

(Trien)Cu(OBz)(OCH₃).—To a stirred mixture of 650 mg (3.0 mmol) of Cu(OBz)(OCH₃) in 50 ml of dry ether under N₂ was added 450 mg (3.08 mmol) of trien. After a few minutes the color of the slurry darkened and became bluish. After stirring for 3.5 hr the dark green slurry was filtered under N₂ pressure and washed twice with dry ether and the excess solvent was removed by pumping at 0.2 Torr. The dark green powder collected (520 mg) was very hygroscopic and formed a sticky green solid on contact with air. For this reason it was not characterized further.

Cu(OCH₃)₂.—A modification of the methods of Finkbeiner and coworkers⁹ and Brubaker and Wicholas²⁹ was used. Into 100 ml of methanol was added 753 mg (2.03 mmol) of Cu(ClO₄)₂·6H₂O. Then with continuous stirring 340 mg (6.28 mmol) of NaOCH₃ was added. A blue precipitate immediately formed and was filtered off under N₂ pressure, and washed twice with methanol and twice with ether. Solvent was removed *in vacuo*, leaving 250 mg of blue powder. *Anal.* Calcd for CuC₂H₅O₂: Cu, 50.6. Found: Cu, 51.5.

(CH₃CHOCH₂NH₂)Cu(OBz).—A solution containing 170 mg (2.26 mmol) of 1-amino-2-propanol in 50 ml of ether was added to 387 mg (2.05 mmol) of CuOBz and stirred under 760 Torr of O₂ for 2.5 hr. The blue solid which formed was filtered off and washed twice with ether. Excess solvent was removed *in vacuo*, leaving 475 mg of product (89% yield). *Anal.* Calcd for CuC₁₀H₁₅NO₃: Cu, 24.6. Found: Cu, 24.0.

Oxidation Runs. Kinetics. Apparatus.—The apparatus for measurement of oxygen was designed to measure small changes in pressure under conditions of nearly constant total pressure. The apparatus consisted of a Pyrex glass reaction vessel equipped with a magnetic stirring bar, an electrically operated solenoid valve, a 3-l. stainless steel gas cylinder, a Wallace and Tierman precision pressure gauge, a Pace-Wianko differential pressure transducer with full scale deflection adjusted to follow a pressure drop of 10 Torr, and a recorder connected to the transducer. The reaction vessel was connected to one port of the transducer and *via* the solenoid valve to the 3-l. reservoir, pressure gauge, and reference port of the transducer. The reaction vessel, transducer, and reservoir were immersed in a constant-temperature bath. A pair of micro switches on the recorder were used to turn the solenoid valve off and on. Whenever 10.0 Torr of oxygen was consumed in the reaction vessel the solenoid opened and allowed the vessel to equilibrate with the reservoir. When zero differential pressure was reestablished the solenoid closed. The times for equilibration were generally small compared to the consumption times. The gas volume in the reactor was calibrated so that the moles of oxygen consumed and the rates of oxygen uptake were calculated from the slopes of the recorder plots. The slopes were much more accurate than total oxygen consumption, since the errors in each pressure cycle accumulated in the total consumption. In duplicate experiments maleic anhydride was hydrogenated very slowly and the total hydrogen consumption was exactly the theoretical within $\pm 0.4\%$. However, in the oxidation experiments where consumption was fast, the total consumption usually fell short of theoretical.

Procedure.—All runs were at 25.0°. Pyridine-methanol (5:1, v/v) was the solvent in all cases except where mentioned. The hydrocarbon and amine were dissolved in the solvent. The catalyst was placed in a polyethylene boat which was suspended above the solution. The vessel was sealed and pumped and filled four times with pure O₂ at the desired pressure. After the reservoir was connected, the solution was then stirred until no more pressure change occurred; the solution then had attained the equilibrium oxygen concentration. The catalyst was added and the rate of pressure drop was followed. During a typical run the total pressure was 1000 Torr and pressure changes of 10.0 Torr were followed per cycle. After complete reaction the total drop in the reservoir was about 1–2 Torr. The vapor pressure of the solvent was measured and found to be 50 (± 1) Torr. Thus the

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total pressure of O₂ above the reaction was just the total pressure minus 50 Torr. The stirring speeds were adjusted to avoid making the rates diffusion controlled. In rates higher than about 150 M min⁻¹ diffusion rates of oxygen begin to compete as rate-limiting steps. All kinetic studies were done below this limiting rate.

Products.—Reaction solutions were quenched by pouring into cold 1 M HCl. The mixture was extracted with two portions of benzene and the benzene extracts were washed several times with water. The benzene solutions were dried and analyzed by gas chromatography. Fluorene, fluorenone, and fluorenone were determined on an XE-60 column at 230° using chloronaphthalene as an internal standard. No fluorenone was found in any reactions.

9,9'-Bifluorenyl was analyzed on an XE-60 column (seasoned overnight at 275°) at 245°.

Spectra.—Visible spectra were done using a Cary 14 spectrophotometer. A Varian Aerograph instrument was used for esr spectra except for liquid helium temperatures, where a super heterodyne spectrometer operating near 9200 MHz was used.

Registry No.—Fluorene, 86-73-7; CuOBz, 14604-51-4; Cu(Cl)(OCH₃), 2850-63-7; Cu(OBz)(OCH₃), 34825-83-7; (trien)Cu(OBz)(OCH₃), 34825-62-2; Cu(OCH₃)₂, 1184-54-9; (CH₃CHOCH₂NH₂)Cu(OBz), 34825-84-8.

The Chemistry of Blocked Isocyanates. II. Kinetics and Mechanism of the Reaction of Dibutylamine with Phenyl and 2-Methylphenyl Oxime Carbamates¹

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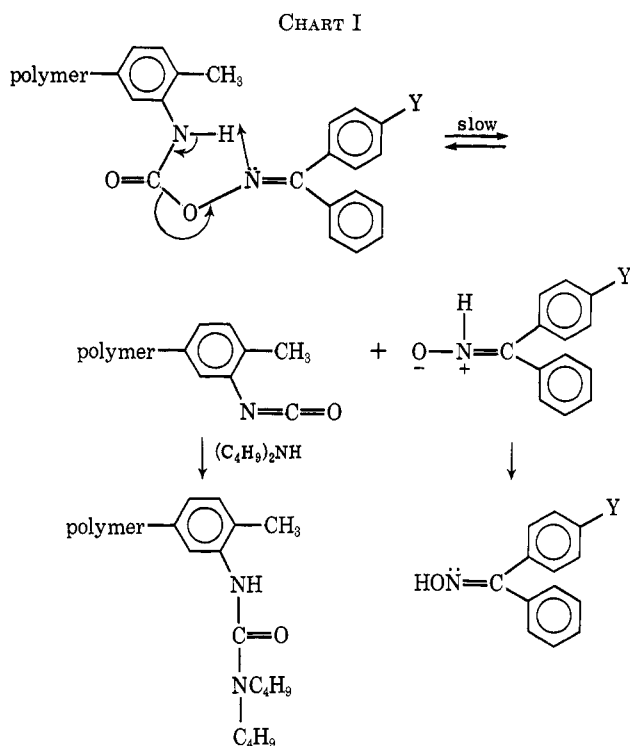
Dibutylamine reacts with carbamates derived from substituted benzophenone oximes and phenyl isocyanates. The reactions follow first-order kinetics and the products are the corresponding substituted phenyldibutylureas and the oximes. The rate constants for reaction of para-substituted phenyl carbamates are insensitive to added excess amine. Activation parameters for the unsubstituted compound are $\Delta H^\ddagger = 25.7 \pm 0.3$ kcal mol⁻¹ and $\Delta S^\ddagger = -0.24 \pm 0.39$ eu. The reaction is facilitated by electron-withdrawing isocyanate substituents ($\rho = +0.296 \pm 0.012$, $r = 0.995$, correlation with σ) and by electron-donating oxime substituents ($\rho^+ = -0.401 \pm 0.011$, $r = 0.997$, correlation with σ^+). The rate constants for carbamates derived from 2-methylphenyl isocyanate and substituted benzophenone oximes also increase with increased electron-donating ability of the substituents ($\rho = -0.512 \pm 0.034$, $r = 0.979$, correlation with σ). The difference in mode of the substituent effect is interpreted as indicating the intervention, in the former case, of a zwitterionic intermediate in the otherwise concerted carbamate dissociation.

In a previous communication,¹ we reported on the unblocking of benzophenone oxime-blocked polyurethanes using dibutylamine as coreactant. It was found that the reaction followed first-order kinetics and was not subject to base catalysis. Unlike the similar reaction of phenol-blocked polyurethanes^{2,3} whose rates are favored by electron-withdrawing substituents on the blocking group, the reaction studied was found to be accelerated by electron-donating oxime substituents. On the basis of this evidence and the near-zero entropy of activation for this reaction, we postulated a five-center cyclic, intramolecular transition state for the decomposition as shown in Chart I.

In order to investigate further the postulated mechanism, we undertook to study oxime unblocking of model compounds. Two series of compounds, based on phenyl and 2-methylphenyl isocyanate (Charts II and III) were synthesized. Rate constants were determined for reaction of these compounds with dibutylamine in toluene solution. This paper discusses the results of these experiments and their bearing on the intramolecular transition state.

Experimental Section

Melting points were determined on a Mel-Temp apparatus and are uncorrected. Infrared (ir) spectra were taken in KBr using a Perkin-Elmer Model 457 instrument. Nuclear Magnetic



Resonance (nmr) spectra were recorded on a Joelco Minimar at ambient temperature in perdeuterioacetone solution. Tetramethylsilane (also deuterated solvents from Stohler Isotope Chemicals) was used as internal standard. Microanalyses were by Micro-Analysis, Inc., Wilmington, Del.

Benzophenone, substituted ketones, hydroxylamine hydrochloride, phenyl isocyanate, and 2-methylphenyl isocyanate were used as received from Eastman Organic Chemicals. Pyridine and dibutylamine were distilled from KOH. All inorganic

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