Chemistry of Phenoxo Complexes. I. On the Mechanism of Decomposition of Phenoxocopper(II) Complexes

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*Contribution from the Chemistry Department,
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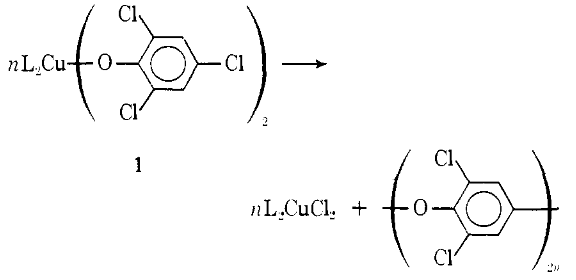
Abstract: The thermal decomposition of bis(2,4,6-trichlorophenoxo)bis(pyridine)copper(II) (**1**) in solution does not occur spontaneously, but is induced by oxygen, or free-radical initiators. No radicals are detected until the disappearance of **1** is complete. After **1** has disappeared, phenoxy radicals slowly build up in the system to a maximum and then decay again. The disappearance of **1** is preceded by an induction period, which may be extremely long in uninitiated reactions, but this induction period is markedly diminished by free-radical initiators. The induction period is followed by a marked autoacceleration, indicative of a branched chain process. The above observations are interpreted in terms of a mechanism with the following key step: (1) fast induced decomposition of **1** by a radical to give a Cu(I) complex and a radical-substituted 2,4,6-trichlorocyclohexadienone, **3**; (2) slow dissociation of **3** into the initiator radical and a 2,4,6-trichlorophenoxy radical (chain branching); (3) abstraction of a chlorine atom from **3** by Cu(I) to give $Cu^{II}Cl$ and a substituted phenoxy radical. The efficient initiation of the decomposition of **1** by CCl_4 and CBr_4 is attributed to charge transfer, or atom transfer between the carbon tetrahalide and coordinated phenoxide. Although trihalomethyl radicals efficiently abstract chlorine from **3**, they do not diminish the polymer molecular weight by combining irreversibly with phenoxy radicals.

In biological systems, copper-containing enzymes play a central role in the synthesis, modification, and removal of the intricate hierarchy of regulatory phenolic amines and phenolic amino acids.[1,2] Copper complexes have also proved effective for catalytic oxidative coupling of phenols *in vitro*, and are used commercially for production of high molecular weight poly(phenylene oxides), diphenoquinones, and 4,4′-biphenyldiols.[3]

The extremely short lifetimes of metal-containing intermediates in these catalytic reactions make their detection and study extremely difficult. Consequently, although great progress has been made in understanding the manner in which products arise from reactions of phenoxy radicals,[4–11] very little is known of the primary processes which generate the phenoxy radicals.

The synthesis of stable phenoxocopper(II) complexes, able to undergo thermal decomposition to poly(phenylene oxide), presented an opportunity to study the primary production of phenoxy radicals from such species.[12,13] The stoichiometry first reported for these reactions (eq 1)[12,13] was deceptively simple and has been revised to account for observed autoxidation of solvent and copper complexes, and for the finite molecular weights of the polymers produced.[14]



1

2

(1)

Tsuruya, *et al.*, have studied the decomposition of tetrakis(trichlorophenoxo)-μ-bis(hexamethylphosphoramide)dicopper(II) in the solid state.[15] Although little information on mechanism was obtained, the appearance and disappearance of phenoxy radicals were directly observed by esr. In the present paper we present the results of a study on the solution decomposition of bis(2,4,6-trichlorophenoxo)bis(pyridine)copper(II) (**1**).

Results

Initial Observations. During the early phases of this investigation, attempts were made to follow reaction 1 gravimetrically. A series of solutions was prepared under carefully controlled conditions under vacuum and subjected to a sequence of increasing decomposition times. Extents of reaction were determined by measuring the amount of product copper complex and the amount of polymer produced. Initial runs gave extremely erratic results. By using spectroscopic grade solvent that had been freshly distilled from calcium hydride and a sample of **1** that had been recrystallized twice, the data shown in Figure 1 were obtained. In addition to the considerable scatter of the data, there is strong evidence for an induction period during which no product copper complexes are formed.

In a final series of reactions where the complex was further recrystallized, only the middle third of the vacuum-distilled solvent was used and the vacuum line

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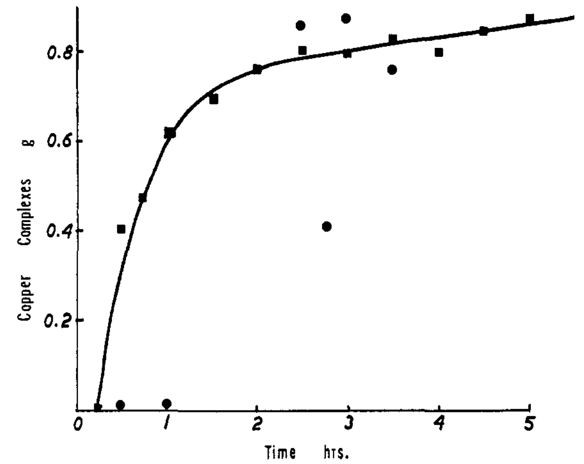

Figure 1. Rate of appearance of product copper complexes on decomposition of **1**: (●) in benzene under vacuum; (■) in toluene in air. Concentration of **1**: 40 g/l., T = 85°. The large scatter in vacuum and small scatter in air, such as shown in this figure, were observed many times and were independent of solvent.

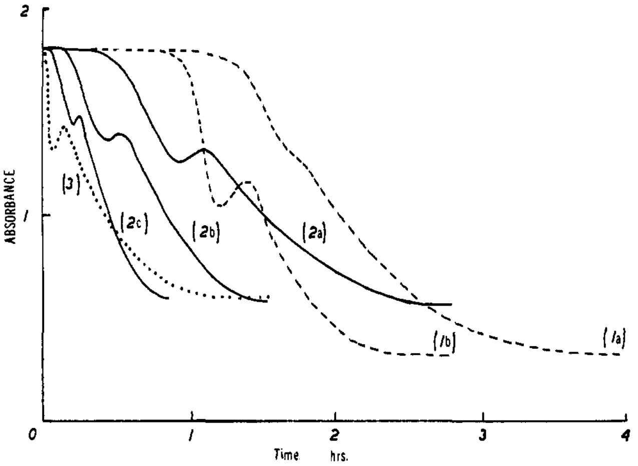

Figure 2. Time dependence of the absorbance of **1** at 22,500 cm^{-1}: (1) benzene at (a) 70° and (b) 75°; (2) toluene at (a) 70°, (b) 85°, and (c) 90°; (3) cumene at 70°. Initial concentration of **1**, 0.0014 *M*.

was cleaned and thoroughly flamed before use; no decomposition of **1** occurred at 85° over a period of 7 days. One of these samples was deliberately contaminated with carefully dried air and a second with carefully deoxygenated water vapor. The aerated sample had decomposed after 3 hr at 85°, but the water-contaminated one did not decompose.

When runs similar to those described above were carried out in air, the behavior was much more consistent and reproducible. An example of such a run is also shown in Figure 1.

Spectrophotometric Observations. The reactant **1** has a strong absorption band, with a maximum at 22,500 cm^{-1}, which obeys Beer's law. The decomposition of the complex in solution is readily followed by monitoring this band. Some absorbance *vs.* time curves are shown for the reaction in benzene, toluene and cumene, at several temperatures, in Figure 2. These reactions were carried out with no precautions to exclude air from the system.

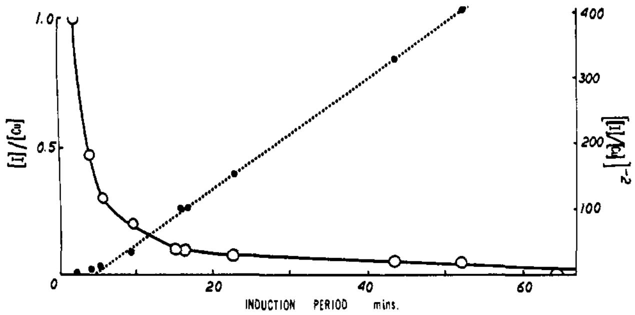

Figure 3. Dependence of induction period on initiator concentration [I] (○) and [I]$^{-2}$ (●). Concentration of **1**, 0.0014 *M* in toluene. Reaction temperature, 80°. Initiator, benzoyl peroxide.

Three features are notable in Figure 2: the long induction period at lower temperatures, the rapid acceleration after onset of reaction, and the inflexion, or even pronounced maximum, through which the absorbance passes at intermediate stages of reaction. In addition, it should be pointed out that the residual absorbance after apparent complete reaction is due in part to the presence of a trace of μ_4-oxocopper(II) complex[14] and partly to absorption by the polymer. The absorption of the polymer at 22,500 cm^{-1} is considerable for low molecular weight, highly branched material and negligible for high molecular weight, less branched material.[16]

There is a notable reduction in the induction period in passing from benzene, to toluene, to cumene at 70°. This feature is in line with the increasing ease of autoxidation of the solvent and the initiating role of organic radicals in this reaction. The initiation of the reaction by some common initiators and the dependence of the composition of the product copper complex on solvent autoxidation has been described elsewhere.[14]

The effect of benzoyl peroxide concentration on the induction period was investigated by following the reaction spectrophotometrically, and some results are presented in Figure 3. A plot of [initiator]$^{-2}$ *vs.* induction period is also included in this figure since this is the only simple function which gives a linear correlation.

Electron Spin Resonance Spectroscopy. The decomposition of **1** and the appearance of **2** in toluene under an atmosphere of air at 100° are easily monitored by following the esr spectra of the two complexes. Changes in the esr spectrum due to Cu(II) are shown in Figure 4. After most of the complex **1** had converted to **2** (time > 60 min), a small blip was observed at 3250 G. Increasing the gain 100-fold revealed the existence of a very sharp singlet (g = 2.007) due to an organic radical. The intensity of this signal continued to grow, essentially linearly, for many hours after changes in the Cu(II) spectrum had ceased. A comparison of the radical signal strength with the optical absorbance of a sample subject to decomposition under the same conditions is shown in Figure 5. The optical experiment corroborates the esr evidence that the radical signal appeared only *after* the transformation of the copper complex was essentially complete.

After standing for 5 days at 100°, the radical signal was no longer detectable.

A second reaction was performed in benzene at 70° in

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(16) For a detailed discussion of the properties of the polymers, see part II of this paper: B. Carr and J. F. Harrod, *Macromolecules*, in press.

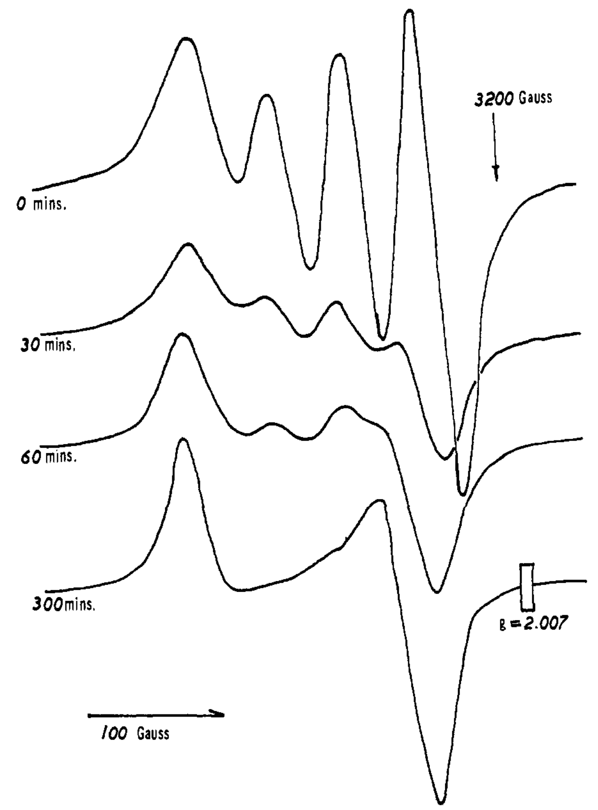


Figure 4. (a) Dependence of Cu^{II} esr spectrum on reaction time. (b) The 300-min curve at $g = 2.007$ amplified × 100.

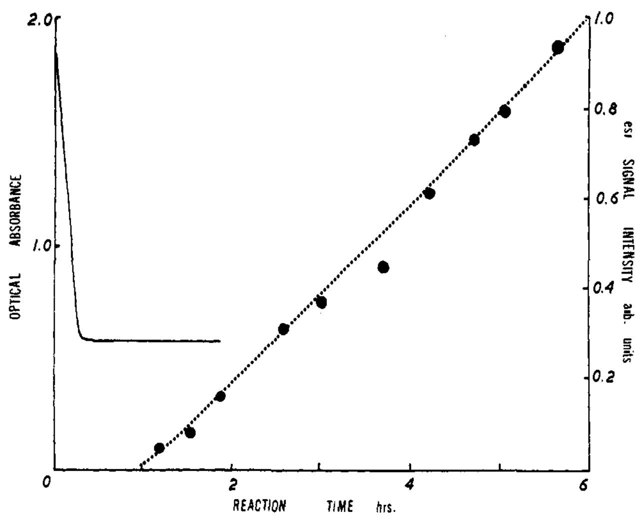


Figure 5. Comparison of optical absorbance (——) and esr signal strength (----) for decomposition of **1** under comparable conditions.

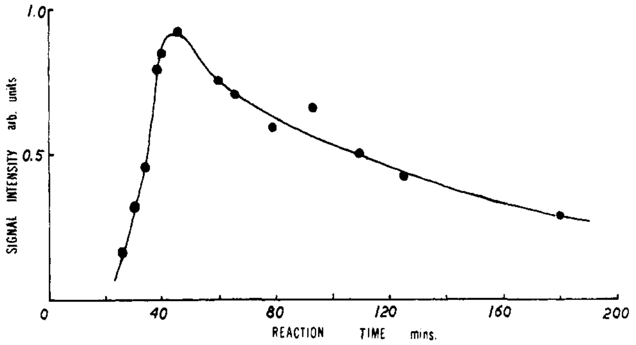


Figure 6. Variation of phenoxy radical signal strength with reaction time for a CCl_4 accelerated reaction.

the presence of carbon tetrachloride ($Cu:CCl_4 = 1:1$). The whole reaction was greatly accelerated and both growth and decay of the radical signal were observed, as shown in Figure 6. Again, the point at which the radical signal begins to grow occurs after the conversion of **1** to **2** is complete.

Catalysis by Carbon Tetrahalides. In the course of studying the effects of typical radical transfer agents on the decomposition of **1**, it was discovered that carbon tetrahalides have an extraordinary capacity to promote the reaction. For example, carbon tetrabromide in a molar ratio of 1:1 with respect to **1** was about as effective as a 10:1 molar ratio of benzoyl peroxide at 70°. Similar behavior was observed for carbon tetrachloride.

Both the copper halide and the polymer from a decomposition of **1**, in the presence of a tenfold molar excess of carbon tetrabromide, were analyzed for bromine. The copper complex was found to contain 23% chlorine and 4% bromine, suggesting a mixture of approximately 90% Py_2CuCl_2 and 10% Py_2CuBr_2. No bromine was detected in the polymer by elemental analysis.

After removal of the copper complexes by filtration and precipitation of polymer by addition to methanol, the residual liquor was concentrated and analyzed by tandem vpc–mass spectrometry. A substantial amount of CBr_3Cl was detected in the product, the chromatogram peak area for CBr_3Cl being roughly one-tenth of that for CBr_4.

The molecular weights of polymers produced in the presence of CBr_4 and CCl_4 were identical with those produced in the absence of these additives. A set of three runs under identical conditions (reaction time, 68 hr; concentration, 50 g/l.; 70° in benzene), except that one contained no additive, a second contained CCl_4, and the third CBr_4, yielded polymers with number average molecular weights of 49,000, 49,000, and 46,000, respectively.

Discussion

The salient experimentally observed features of reaction 1 which require explanation by any mechanism are the following.

(a) The reaction does not occur in the absence of initiators.

(b) Oxygen can initiate the reaction, but there is a substantial induction period.

(c) Free-radical initiators reduce the induction period and accelerate the reaction. No initiator fragments are detectable in **2**.[14]

(d) The end of the induction period, which may be hours or even weeks, is characterized by the onset of a rapid autoacceleration.

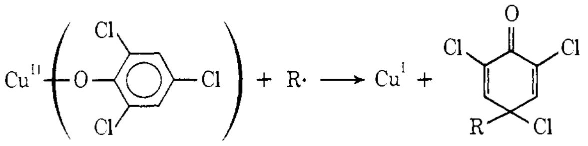
(e) There is a reaction intermediate which is a strong chromophore at 22,500 cm^{-1}.

(f) No phenoxy radicals are evident in the reaction medium until after the transformation of **1** into **2** is complete, after which a steady increase in radical concentration is observed.

(g) The growth of polymer molecules is stepwise and continues long after the transformation of **1** into **2** is "complete." Polymer molecular weight asymptotically approaches a limit with time.[16]

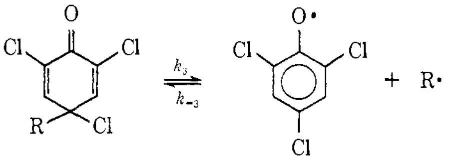
(h) Carbon tetrahalides initiate the reaction but do not affect the molecular weight of the polymer. Halide from the initiator is incorporated into the product **2**.

A combination of (a), (c), and (f) leads to the conclusion that radicals must attack **1** in a fast reaction to produce nonradical products. The most plausible reaction which satisfies these criteria is shown in reaction 2. Cyclohexadienone derivatives, **3**, are well known to result from dimerization of phenoxy radicals and a great deal is known of their thermodynamic and kinetic stability.[11,17,18] Reaction 2 is an example of electron transfer through an extended bridge.[19]



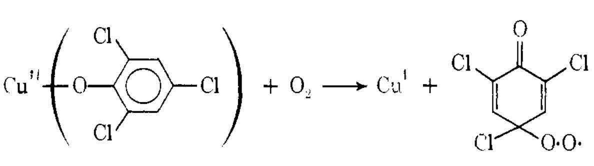
3 (2)

The intermediate **3** is attractive so far as its properties provide a natural explanation for two further key features of the overall reaction. Firstly, **3** is expected to absorb strongly in the visible region and is a good candidate for the strong transient chromophore evident from studying the reaction spectrophotometrically. Secondly, the known dissociation of **3** into its precursor radicals[11,17] provides an explanation for the feature (d). A combination of reactions 2 and 3 provides a radical chain branching which doubles the number of available radicals after each radical-induced dissociation of **1**. Although specific values for k_3, relevant to the intermediates involved in the present reaction, are unknown, the known rates for analogous reactions suggest that the forward reaction of 3 could be slow enough to account for the slow buildup of radicals after depletion of **1**.[11] As long as there is any **1** in the system, it acts as an effective radical scavenger.



(3)

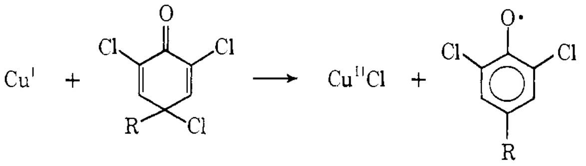
By analogy with (2), oxygen may function as an initiator by formation of a 4-peroxycyclohexadienone as in (4). Such peroxides are undoubtedly intermediates in the formation of bis(substituted cyclohexadienonyl) peroxides by reaction of oxygen with phenoxy radicals.[20]



4 (4)

Little can be said at the moment of the mechanism whereby carbon tetrahalides initiate the reaction. Not unexpectedly, chemical analysis reveals no evidence of bromine in the polymer produced in the presence of CBr_4. An activation analysis study, which might be more conclusive, has not been carried out to date. The two most likely modes of action of the carbon tetrahalides are induction of decomposition of **1** either by halogen atom transfer to coordinated phenoxide, or by charge transfer complex formation between CX_4 and coordinated phenoxide.

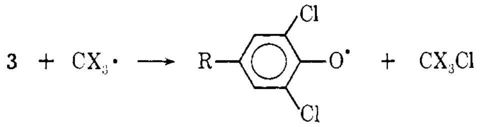
The formation of Py_2CuBr_2 and CBr_3Cl and the failure of added CBr_4 to lower the molecular weight of the polymer formed show that, in addition to acting as initiators, the carbon tetrahalides also act as very effective radical chain carriers. In the absence of carbon tetrahalide, radical regeneration from quinol ether, **3**, occurs by halogen atom transfer to Cu^I generated in (2), thus



(5)

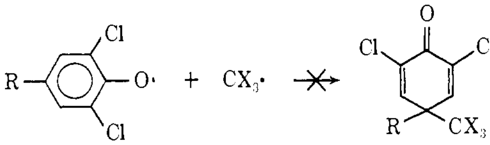
In the presence of CX_4, there is competition between the additive and **3** to transfer a halogen atom to Cu^I. The amount of Py_2CuBr_2 formed in the presence of CBr_4 suggests that transfer from **3** is much more rapid. The constancy of the molecular weight indicates that the trihalomethyl radicals from CX_4 halogen transfer are very efficient in picking up halogen from **3** to regenerate phenoxy radicals. The redox cycle whereby CX_4 participates as a radical chain propagator is analogous to that which occurs during the copper-catalyzed addition of CX_4 to olefins,[21,22] and is represented by the sequence of eq 2, 6, and 7.

$$Cu^I + CX_4 \longrightarrow Cu^{II} + CX_3\cdot \quad (6)$$



(7)

The fact that the molecular weight is insensitive to the presence of CX_4 excludes the possibility of coupling between phenoxy and trihalomethyl radicals (eq 8), at least as a unidirectional process, since it leads to a diminution of the halogen scavenging capacity of the system. The high selectivity of the trihalomethyl radicals for abstraction of Cl, rather than coupling, is undoubtedly due to their great steric encumbrance.



(8)

According to the proposed mechanism, the early phase of the reaction involves the formation of a supra-equilibrium concentration of **3** which branches the kinetic chain by decomposing to radicals more slowly than they react with **1**. During this period the concentration of Cu^I also rises until its rate of abstraction of halogen from **3** equals its rate of production. The concentrations of Cu^I and of **3** are equal if one ignores the occurrence of side reactions. The features of this

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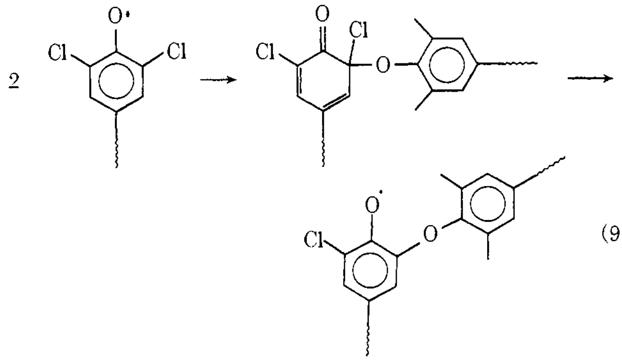
reaction correspond to those described by Semenov[23] as "degenerate branching," the potentially explosive character being limited by the relative slowness of reactions 3 and 5. We have not thus far been able to reconcile the apparent inverse square dependence of the induction period (*cf.* Figure 3) with a simple branched chain mechanism with a constant rate of initiator radical generation.

The rate of dissociation of **3** must be slower than its reaction with Cu^I, otherwise large amounts of Cu^I would accumulate in the system, a result which is not supported by the esr evidence. On the other hand, if the maximum which appears in the optical absorbance at midreaction is due to accumulation of **3**, there must be a tangible amount of Cu^I present. Further evidence that dechlorination of **3** is faster than its dissociation into radicals is the fact that polymer of significant molecular weight appears in the system well before complete reaction of **1**.

Beyond a certain point in the reaction, the concentration of **3** and Cu^I must begin to diminish again due to the demands of mass balance. The more Py_2CuCl_2 that accumulates, the less copper there is available to be in the form of Cu^I. The esr evidence shows that propagation of polymer chains occurs almost entirely by reaction of polymeric radicals with **1** until the reaction is very far advanced. Axiomatically, this requires that the radical chain branching reaction (3) produce one polymer radical and one trichlorophenoxy radical. The very sharp esr signal at $g = 2.007$ can be assigned with reasonable certainty to a phenoxy radical.[15,24–26] It is likely that, at the resolution used in our experiments, the polymer and trichlorophenoxy radicals would not be resolved. Beyond "completion" of the decomposition of **1** there is presumably a slow redistribution reaction, but there must also be a polymer radical coupling reaction to account for the near doubling of $\bar{M}_n$ between "completion" of the reaction of **1** and the completion of polymer growth. This reaction may be identified with the polymer branching reaction that is known to occur in these systems [reaction 9].



(9)

Nmr evidence proves, however, that the branching density at the earliest stages of reaction is not significantly lower than after long reaction times, and therefore branching is certainly not confined to the later stages of reaction. The intramolecular coupling of **5** to form a dioxin may play a role in kinetic termination in this reaction, as previously suggested by Golden.[27]

Conclusions

The chemistry of the reaction represented by eq 1 is one of extraordinary complexity. This complexity is due to a combination of extrinsic, and potentially avoidable, factors such as adventitious initiation, concurrent solvent autoxidation and hydrogen transfer from solvent, or free phenol present as impurity, and intrinsic factors, such as the inherent kinetic complexity of branched chain reactions.

The present work, together with the large body of previous literature on phenoxy radical chemistry, has mapped out the general features of reaction 1 to the point where a reasonable mechanism may be proposed. This mechanism explains all of the known qualitative features of the reaction and is amenable to quantitative tests, *provided* that the extrinsic factors can be controlled. The evidence to date suggests that these factors are controllable, and work is presently continuing in this laboratory to establish the proposed mechanism on a quantitative basis.

Experimental Section

The copper complexes used in this work were prepared and characterized according to previously described methods.[13]

All solvents were of reagent grade and freshly distilled from calcium hydride. Only the middle half was used.

Decomposition under Vacuum. A sample of solid **1** was placed in a 200-ml round-bottom flask and evacuated on a standard vacuum line. A known volume of solvent, which had been previously outgassed at less than 0.001 Torr, was distilled onto the complex and the vessel sealed off. When necessary, several such vessels could be filled at the same time and under identical conditions.

The reaction mixtures were kept at liquid nitrogen temperature until required and then they were decomposed by immersion in a constant-(±0.5°) temperature oil bath for the required period of time.

Decomposition in Air. Bulk decompositions in air were performed by first preparing a large volume of standard solution. This solution was then divided into several equal portions and dispensed into lightly stoppered erlenmeyer flasks. Decomposition was effected as described above.

Spectrophotometric studies of the decomposition of **1** were carried out with a Hitachi-Perkin-Elmer Model 124 spectrometer equipped with a temperature control unit. The reaction was monitored by following changes in the absorption at $22{,}500\ cm^{-1}$. A standard solution concentration of 0.0014 M was used in Teflon stoppered TSL-Far UV cells, with a small air space to allow for solvent evaporation. The small amount of **2** formed in the reaction quickly settled to the bottom of the cell and did not interfere with measurement of the solution optical density.

Esr spectra were measured with a Varian E-3 spectrometer, fitted with a variable-temperature cavity. A standard solution of **1**, 0.08 M, was used in quartz tubes and the instrument was calibrated with strong pitch. Standard operating conditions were: frequency, 9.17 GHz; power, 300 nV; field set, 3230 G; modulation amplitude, 1 G; modulation frequency, 100 kHz; time constant, 1.0 sec; scan time, 4 min [copper(II)], 30 min (phenoxy radical).

Recovery of Reaction Products. The complex **2** is completely insoluble in reaction solvents and normally precipitates in a coarse, crystalline form that can be easily separated by filtration.

After removal of **2**, the polymer was precipitated by slowly running the solution into a large excess of methanol containing a little concentrated HCl. The polymers were isolated by filtration and dried overnight in a vacuum oven at 100°.

Detailed characterization of the polymers produced in this work has been described elsewhere.[16]

Two reactions, performed in the presence of CBr_4, were further analyzed for products related to the latter additive. After removal

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of 2 and polymer, the methanol-benzene mixture was reduced in volume to 25% of the original on a rotary evaporator. The residual solution was analyzed on an LKB-9000 gas chromatograph-mass spectrometer. The chromatograph was fitted with a 6 ft × 0.5 in. glass column packed with 3% OV-1 on high performance Chromosorb W, and operated at a helium flow rate of 30 ml/min with a programmed temperature of 5°/min from 90 to 200°.

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Nuclear Magnetic Resonance Spectroscopy. Nitrogen-15 and Carbon-13 Spectra of Complexes of Ethylenediaminetetraacetic Acid (EDTA) with Closed-Shell Metal Ions[1]

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Abstract: The ^{15}N and ^{13}C chemical shift changes have been determined for ethylenediaminetetraacetic acid (EDTA) as the result of changes in pH and complex formation with closed-shell metal ions. The carboxyl-carbon ^{13}C shifts in parts per million resulting from complex formation with metal ions are generally smaller than the concomitant shifts of the ^{15}N resonances which themselves are not large. The comparatively small ^{15}N chemical shift changes of EDTA upon metal complex formation are probably due to near-cancellation of variations in local paramagnetic and diamagnetic shielding terms. This may be a general phenomenon for ligands lacking a large local paramagnetic contribution to the shielding of the nitrogen donor atoms.

The binding of metal ions to amino acids and proteins is a subject of very considerable biochemical importance into which studies using nuclear magnetic resonance (nmr) spectroscopy can be expected to lead to significant insight. For initial studies by ^{13}C and ^{15}N nmr spectroscopy of the interactions of amino acids and proteins with metal ions, ethylenediaminetetraacetic acid (EDTA) provided a quite convenient model system. EDTA is an outstanding complexing agent for metal ions,[2] and a great deal of information is available about its complexes. Much of this has come from proton nmr spectra,[3-10] although a ^{23}Na nmr study of the Na(I)-EDTA complex has emphasized the importance of nitrogen binding in the complexation of sodium.[11]

Because the protons of the EDTA ligand are more distant from the atoms intimately involved in bonding to the metal ion, it seemed possible that ^{13}C and ^{15}N nmr spectroscopy of metal-EDTA complexes would reveal effects that do not appreciably affect proton nmr spectra. This expectation is heightened by the presence of the 2p electrons of carbon and nitrogen, which allows for paramagnetic contributions to the nuclear shielding[12] and makes for the much larger chemical shift ranges of ^{13}C and nitrogen nmr by comparison with proton nmr.[13-15]

Results and Discussion

Chemical Shifts. There was some initial controversy over the sites of protonation of EDTA tetraanion;[2] later studies by proton nmr strongly indicated that the first two protons added to the tetraanion primarily go on to the nitrogens.[3,16,17]

To check this conclusion, we have measured the ^{13}C chemical shift changes of the carboxyl group upon protonation of acetate ions, glycinate ions, and the tetraanion of EDTA. These data are given in Table I and support the conclusions drawn by earlier workers from proton nmr results. The key finding here is that the upfield shifts of the carboxyl ^{13}C resonance upon pro-

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