

Registry No.—L·, 29897-74-3; L₂, 1707-68-2.

Acknowledgments.—The authors wish to express their appreciation to R. Dessauer, L. Cescon, and C. Yembrick for bringing the present problem to their attention and for supplying most of the compounds

used in this study. The aid of J. M. White in carrying out these experiments is gratefully acknowledged. We also thank V. F. Hanson for the construction of the flash photolysis apparatus and B. R. Stevens for assistance.

The Biimidazole-Sensitized Photooxidation of Leuco Triphenylmethane Dyes

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Received February 12, 1970

The oxidation of tris(2-methyl-4-diethylaminophenyl)methane by photogenerated 2-(*o*-chlorophenyl)-4,5-diphenylimidazolyl radical (L·) was studied by flash photolysis. An electron-exchange reaction involving L· occurs at an unprotonated amino nitrogen of the leuco dye and is responsible for the first oxidation step. Subsequent reactions do not involve the L· radical and depend only on the structure of the leuco dye and environmental effects. The influence of pH on both the course and rate of the dye-forming reaction is discussed.

Several investigators have studied the nature of the intermediates formed and the reactions which occur when dyes are photoreduced.¹⁻³ The participation of radicals and radical ions in the photoreduction of methylene blue has long been recognized.¹⁻³ Except for the work of Lewis⁴⁻⁷ and Linschitz^{8,9} and a previous publication¹⁰ from this laboratory, little direct evidence has been reported on the nature of the intermediates formed in the oxidation of triphenylmethane leuco dyes or the kinetics of the reactions which they undergo.

The halocarbon-sensitized photooxidation of tris(4-diethylaminophenyl)methane, referred to as leuco ethyl crystal violet (LECV), was recently described and a mechanism presented.¹⁰ Previous papers in this series¹¹ discussed the reactions of the 2-(*o*-chlorophenyl)-4,5-triphenylimidazolyl radicals (L·), formed from the corresponding dimer (L₂), with reducing agents. The present paper is a study of L· induced oxidation of triphenylmethane dyes and their trihydrochloride salts.

Experimental Section

Tris[2-methyl-4-(diethylaminophenyl)]methane (*o*-MLECV), LECV, and their trihydrochloride salts as well as L₂ were prepared by Cescon.^{11a} The solvent CH₃OH was Matheson reagent grade. Linde argon (dry 99.99% pure) was used to deoxygenate all solutions. Spectra were recorded on Cary Model 14 and 15 instruments.

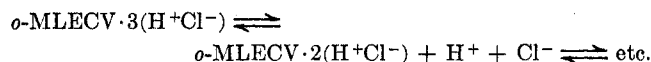
The flash photolysis apparatus was of conventional design and has been described previously.¹⁰ The flash was filtered with a

combination of 0-52 plus 7-60 Corning filters to provide light of (3700 ± 200 Å). The analysis light was appropriately filtered to preclude photolysis of solutions.

The absorption spectrum of the leuco dye radical-ion intermediate was obtained using an apparatus designed by Dr. D. C. Reitz. The methanol solution containing leuco dye and CCl₄ was placed in a rectangular quartz cell and suspended in a cold stream of nitrogen within a multiwalled dewar flask constructed to fit inside the sample compartment of a Cary Model 14 uv-visible spectrometer. Optically flat quartz windows were provided on the dewar flask for analysis. Photolysis was accomplished through a hole in the sample compartment on a direct line with the sample cell. The photolysis light was filtered with a Corning 7-39 filter to prevent photolysis of the intermediate.

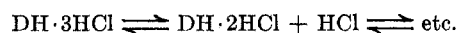
Results and Conclusions

Structure of *o*-MLECV·3HCl and L₂ in Various Solutions.—Ultraviolet absorption spectra of the *o*-MLECV·3HCl + L₂ mixture in methanol revealed no complexing between initiator and leuco dye. (Unless specified otherwise, all work was performed with *o*-MLECV at 6.6 × 10⁻⁵ M and L₂ at 4 × 10⁻⁴ M.) The equilibrium constant *K* at 25° for the reaction



was determined in methanol, glycerol, acetonitrile, and dimethylformamide (Table I). These values were ob-

TABLE I
DEGREE OF PROTONATION AT 25°^a



	<i>k</i> , mol l. ⁻¹	Degree of protonation (statistical structure)
Methanol	4 × 10 ⁻⁵	DH·2.5HCl
Glycerol-methanol 60:40	7 × 10 ⁻⁵	DH·2.4HCl
Dimethylformamide		DH·OHCl
Acetonitrile	~10 ⁻⁷	DH·2.9HCl

^a DH·3HCl = 6.6 × 10⁻⁵ M and L₂ = 4 × 10⁻⁴ M.

tained by comparing the extinction coefficient at 2650 Å of *o*-MLECV·3HCl dissolved in the various solvents with that of the *o*-MLECV free base and of *o*-MLECV·3HCl dissolved in methanolic 0.1 M HCl (Figure 1). It is assumed that the free base extinction coefficient at

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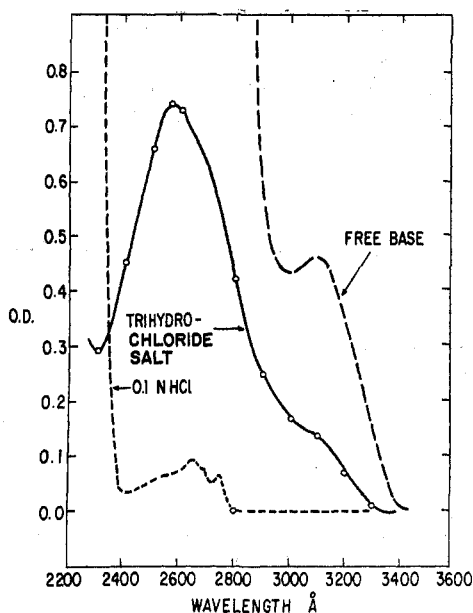


Figure 1.—Effect of acid on the *o*-MLECV ($6.65 \times 10^{-5} M$) spectrum in methanol.

2600 Å is equal to three times the extinction coefficient for an individual 4-diethylaminophenyl structure. The free or available amino group concentration for the salt is calculated from the optical density at 2600 Å, assuming Beers law is obeyed. These data allow a calculation of the statistical degree of protonation and, as will be shown later, have an important effect on the ease of oxidation of the leuco dye. The results may be summarized by noting that in methanol and 60% glycerol-40% methanol only the first of the three deprotonating steps is important with the trihydrochloric salts. In the two hydroxyl-containing solvents the equilibrium is such that an equimolar mixture of di- and triprotonated species is present. In acetonitrile very little dissociation occurs, while in DMF the free base is the major species, quite likely due to the basic character of this solvent.

Quantum Yield of Color Formation vs. Wavelength as a Function of the Absorbing Species.—Table II

TABLE II
COLOR QUANTUM YIELD (Φ_c) vs. IRRADIATING WAVELENGTH^a

Irradiating wavelength, Å	Φ_c^b
2537	0.66
3130	0.49
3660	0.55

^a *o*-MLECV·3HCl was $6.6 \times 10^{-5} M$ in methanol; L_2 was $4 \times 10^{-4} M$. ^b Quantum yield was obtained by correcting for screening by *o*-MLECV·*n*HCl.

contains the experimentally determined color quantum yield (Φ_c) as a function of exciting wavelength. All the yields are identical within experimental error. No effect of L_2 concentration on Φ_c in methanol with 3660-Å irradiation was found (Table III). The Φ_c values in Tables II and III were all corrected for screening due to *o*-MLECV·*n*HCl, implying that only light absorbed by L_2 was effective in producing color. Justification for this was obtained by varying the relative concentrations of *o*-MLECV·3HCl and L_2 such that in one case most of the incident light was absorbed by L_2 and in

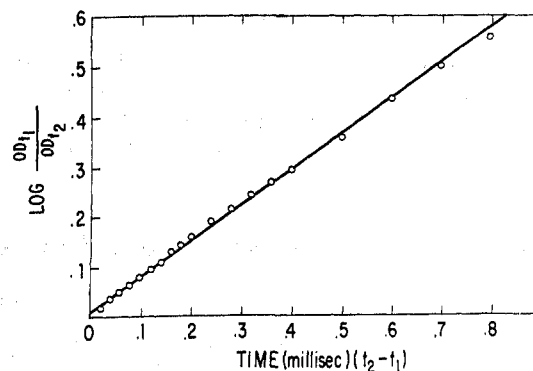


Figure 2.—*o*-Chlorolophine radical decay at 3900 Å in the presence of *o*-MLECV.

TABLE III

Φ_c vs. REACTANT CONCENTRATIONS IN METHANOL^a

Concn, M , <i>o</i> -MLECV·3HCl	Concn, M , L_2	Φ_c^b
6.6×10^{-5}	8×10^{-4}	0.61
6.6×10^{-5}	2×10^{-4}	0.50
6.6×10^{-5}	4×10^{-4}	0.52

^a Photolyzing wavelength was 3660 Å. ^b Corrections for screening by *o*-MLECV·*n*HCl were always applied.

the other most of the light was absorbed by *o*-MLECV·3HCl. Color was produced only in the former case.

The extinction coefficient of *o*-MLECV cationic dye, which is necessary for Φ_c determinations, was obtained by photolyzing a deoxygenated mixture of a known concentration of *o*-MLECV·3HCl with excess L_2 to the point where no more color was formed. The value for ϵ_{6200} obtained in this manner is 11.5×10^4 l./mol cm), and in the event that some dye was photolyzed it represents a minimum value. However, under the condition of the experiment the quantum yield for dye degradation was determined as less than 0.02 compared to $\Phi_c = 0.55$.

Flash Photolysis.—Flash photolysis of LECV- CCl_4 mixtures in methanol and ethanol yielded one observable intermediate.¹⁰ At 4500–4900 Å (called 4600-Å species from now on) an absorption was detected which decayed in about 20 msec to produce the final color (5900 Å). The rate of color formation coincided in both kinetic order and lifetime with the 4600-Å decay. In the present system, initiator fragments should present an additional complication; therefore, the initiation was investigated separately.

L_2 Photolysis.—When L_2 is flash photolyzed in methanol, transient absorptions at 5450 and 3900 Å are detected. Both decay with approximately second-order kinetics, and correcting for differences in extinction coefficient of the lophine radical at 5450 and 3900 Å leads to the conclusion that both absorptions correspond to the same radical species. Whether L_2 is re-formed or whether different products result is not known.

***o*-MLECV Free Base plus L_2 .**—Filters were adjusted to allow only photolysis of L_2 . A transient was observed at 3900 Å, whose decay rate was much faster than the normal lophine radical disappearance rate and, in addition, was first order. At 4660 Å an absorption appeared at a rate and order corresponding to the 3900-Å decay (Figures 2 and 3) thus suggesting

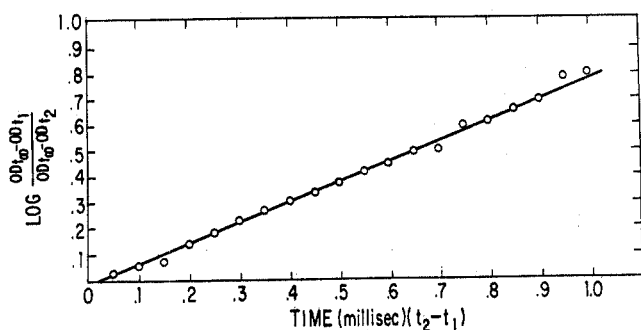


Figure 3.—“4600-Å” formation.

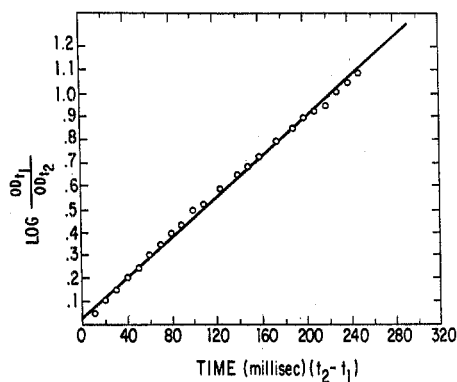


Figure 4.—Decay of “4600 Å” (first order).

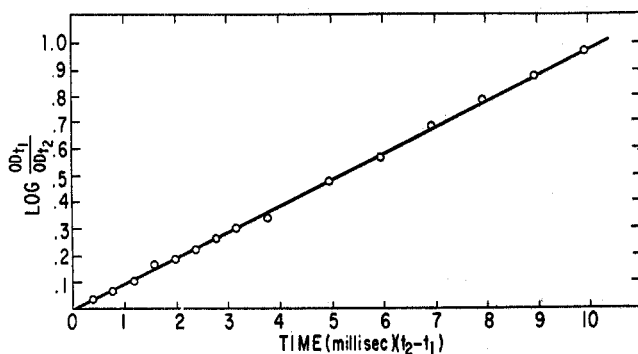
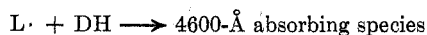


Figure 5.—Reaction of lophine radicals (3900 Å) (first order).

that the 3900 Å reacts to produce the 4600-Å transient. That the observed 3900-Å decay was in reality only pseudo first order was shown by decreasing the *o*-MLECV free base concentration to a point where it was no longer in excess over the concentration of lophine radicals ($L\cdot$). Under these conditions second-order kinetics was observed. The reaction



is in agreement with the results. The true second-order rate constant for 3900-Å ($L\cdot$) decay was obtained by dividing the observed pseudo-first-order rate constant by the concentration of “free amino groups.” The significance of this latter normalization becomes apparent when the data are analyzed with acid in the system. No color is formed when the system *o*-MLECV free base reacts with lophine radicals. The possible reasons for this will be discussed later. The decay at 4600 Å is shown in Figure 4.

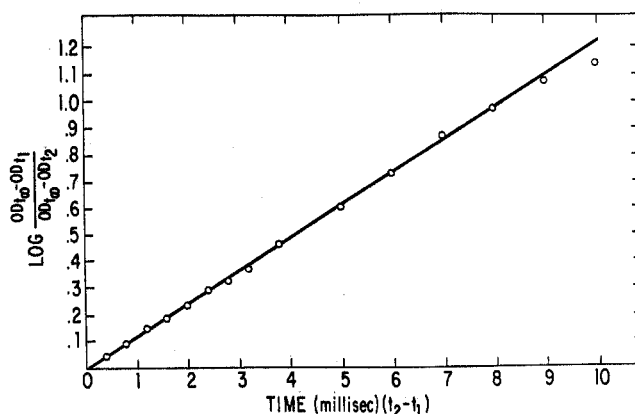


Figure 6.—Formation of “4600 Å” by lophine radicals (first-order kinetics).

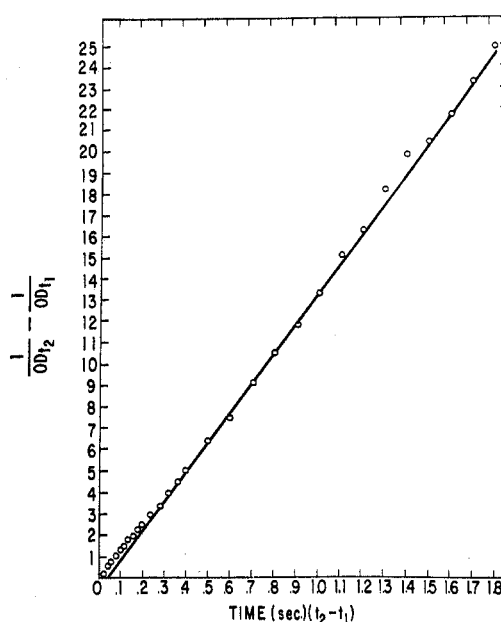


Figure 7.—“4600-Å” decay.

Flash Photolysis of *o*-MLECV·3HCl plus L_2 in Methanol.—When *o*-MLECV·3HCl plus L_2 is flash photolyzed, using light absorbed only by L_2 , the following transient reactions are observed. (a) 3900 Å ($L\cdot$) decays by pseudo-first-order kinetics in a time short compared to the disappearance rate (Figure 5). (b) 4600 Å is formed with a rate and order corresponding to the 3900-Å decay (Figure 6). (c) 6200 Å (color) is formed with a rate and order corresponding to the 4600-Å decay (Figures 7 and 8).

As mentioned earlier, when the trihydrochloride is dissolved in methanol, equilibrium between di- and triprotonated leuco base is established and it is possible to determine the number of protonated and nonprotonated amine functions available for $L\cdot$ reaction by ultraviolet spectroscopy. When the pseudo-first-order rate constant obtained in this system is divided by the concentration of free aromatic amine groups, the true second-order rate constant obtained is identical with that measured for the free base. This quite conclusively points to the amine function as the primary point of attack.

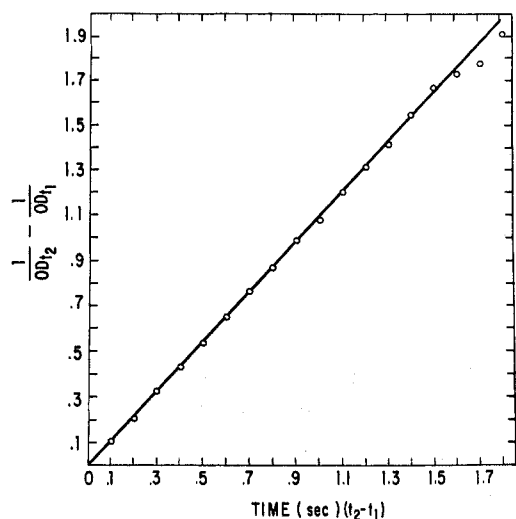
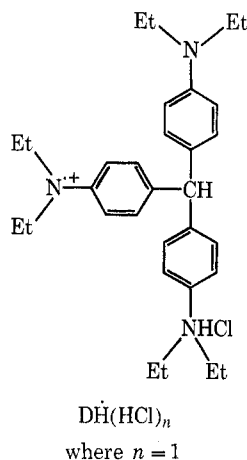
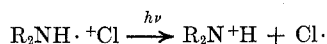


Figure 8.—Color formation.

Since the rate of attack of $L\cdot$ on *o*-MLECV depends on the number of free amine functions, the first intermediate formed would be the radical ion



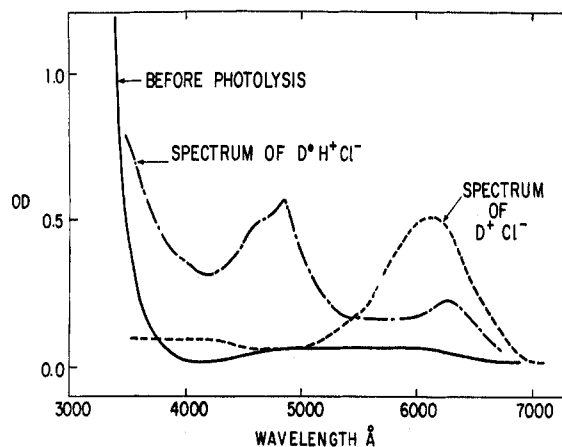
Such radical ions have analogy both in the formation of Würster-type radicals with aromatic diamines and as postulated intermediates in the Hofmann-Löffler reaction



The rapid rate of $L\cdot$ disappearance and its kinetic order, when compared to the slow rate of disappearance of the 4600-Å transient, show the only purpose of $L\cdot$ is to initiate the reaction. Once the electron exchange reaction has occurred, the final dye formation rate depends only on the dye structure and any environmental effects on the 4600-Å intermediate.

Evidence for Identification of the Reaction Intermediates.—Strong evidence that the 4600-Å transient is a radical was obtained by electron spin resonance techniques. Two different means of generating the radical were used.

o-MLECV·3HCl and L_2 were dissolved in methanol and deoxygenated. This solution was circulated through the esr cavity (25°) and irradiated directly. A single line was obtained and could not be resolved. Lophine radicals cannot be responsible, since their rate of disappearance as obtained from the flash photolysis experiments renders their concentration much too

Figure 9.—Absorption spectrum of $D\cdot H^+ Cl^-$ in methanol at -90° .

low. A second method relied on the sensitized decomposition of the *o*-MLECV free base. Free base was dissolved in a 10% carbon tetrachloride–90% methanol solution, cooled to -80° , and irradiated directly in the esr cavity. Again, a single-line spectrum was obtained which could not be resolved. These spectra do not allow a structure to be assigned the radical and do not even prove that the same radical is obtained by either route but they clearly show a radical intermediate that corresponds in lifetime to the optically observed 4600-Å transient intermediate described below.

The optical absorption spectrum of the radical intermediate was also obtained. Figure 9 shows the results of photolysis of *o*-MLECV free base in 10% carbon tetrachloride–90% methanol at -90° . The radical intermediate has two peaks in the vicinity of 4800 Å and apparently one at 6300 Å. On warming the normal 6200-Å absorption of the dye cation forms. Mixing was not possible in the low-temperature cell used in this experiment, and thus extinction coefficient relationships cannot be obtained from Figure 9.

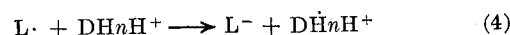
The possibility that the 4800-Å species might be simply a protonated form of the final dye was eliminated by examining the behavior of the dye spectrum as a function of added sulfuric acid. The major change is a shift to longer wavelengths (6700 Å) and then an almost complete loss of the 6700-Å absorption. No absorption at 4800–4900 Å is ever formed by protonation.

The optical spectral data make it apparent why the formation of the 4800-Å transient and the loss of the 3900 Å (lophine radical) could not be followed over their entire range. The marked spectral overlap of the two species at 3900 Å is easily seen in Figure 9.

The Role of Protons in Promoting Color Formation.—Reactions 1, 2, 3, and 4 have been discussed.



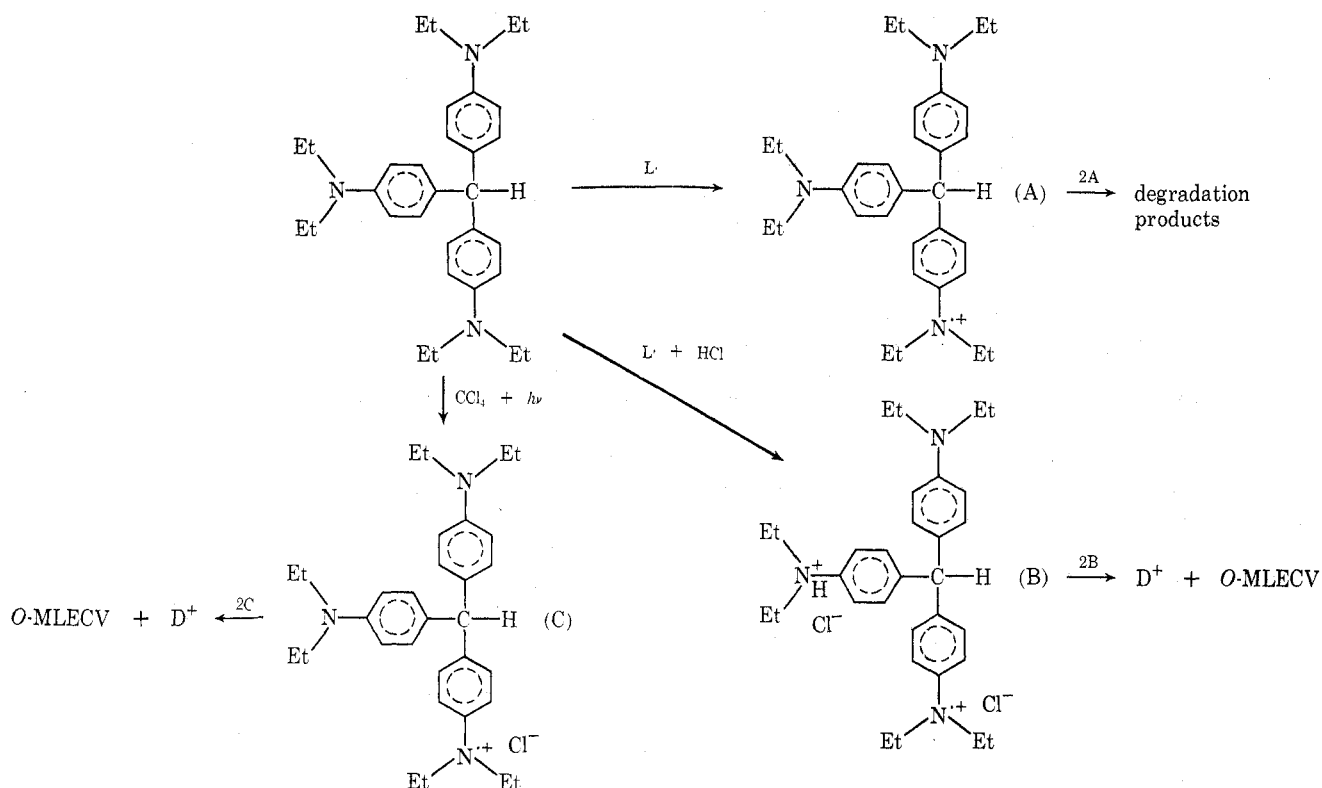
$$\Phi_{\text{dissociation}} = 0.55$$



$$0 < n < 3$$

$$k = 0.83 \times 10^7 \text{ l./mol sec in methanol at } 25^\circ$$

SCHEME I



The question of the degree of protonation of the 4600-Å intermediate and its effect on the rate of color formation will now be explored.

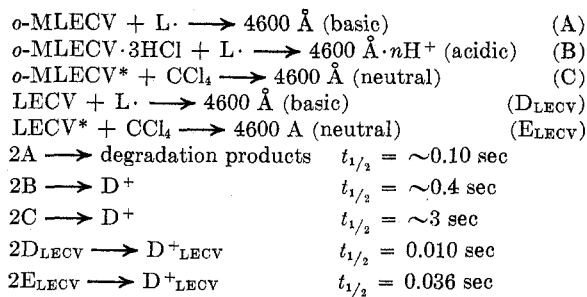
In methanol, the *o*-MLECV·3HCl plus L₂ composition yields a 4600-Å transient that decays by good second-order kinetics with a lifetime of approximately 0.2 sec (Figure 6). When *o*-MLECV free base is photolyzed with carbon tetrachloride as sensitizer, the 4600-Å absorption is formed but decays with a lifetime of approximately 4 sec (first order).¹² However, when *o*-MLECV·3HCl is sensitized with CCl₄, the lifetime of 4600-Å decay again becomes second order with a lifetime of 0.2 sec. These three experiments illustrate the influence of [H⁺] on the observed kinetics as well as the independence of the 4600-Å intermediate from the initiator. They also show that no long-lived complex with lophine radicals is responsible for the 4600-Å transient absorption and its decay rate.

The effect of HCl on this disproportionation is undoubtedly due to the degree of protonation of the intermediate and must be included in the mechanism. With no initial concentration of HCl, the concentration of HCl generated photochemically cannot exceed the final concentration of dye formed, and therefore the minimum degree of protonation would be present. This is the case for CCl₄-sensitized decomposition of the free leuco base.¹²

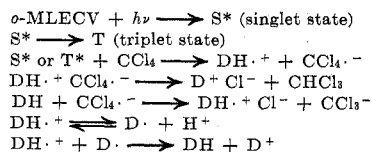
As hydrochloric acid is added to the system (in the form of the leuco trihydrochloride), the rate of attack of

lophine radicals on the dye is decreased, and the rate of disproportionation of the 4600-Å transient is increased. No significant change in color quantum yield occurs; thus, the change in half-life is not a concentration effect. However, when lophine radicals react with *o*-MLECV free base, no color is formed, and its 4600-Å transient disappears with the highest rate. End product analysis showed that the oxidized form of the dye is not present under these conditions. Thus, the effect of acid is twofold: (1) it increases the rate of disproportionation of the 4600-Å transient, and (2) it actually controls the chemical course of the reaction.

To understand these results we need to examine LECV oxidation by L· under neutral conditions. Photolysis of a methanolic solution of L₂ plus LECV gives color (D⁺) with a quantum yield equivalent to the *o*-MLECV·3HCl yield (~0.5). The only difference in structure between the leuco bases is the presence of the three ortho methyl groups in *o*-MLECV. Thus, the most reasonable effect is a steric one that interferes with reaction at the central C-H bond. Since it has already been shown that the 4600-Å transient is a free radical and does disproportionate to form the final products, this too must be considered in the mechanism. Schematically, we can represent the experimental facts as follows.



(12) For reference the scheme for CCl₄ photosensitized oxidation of *o*-MLECV¹⁰ is

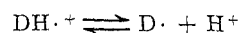


The ortho methyl group steric effect is exhibited in the reduced reactivity of all the species derived from *o*-MLECV vs. LECV. Under basic conditions, LECV yields the final dye. Reactivity of the ortho methyl groups of *o*-MLECV might explain the results if disproportionation occurred at these groups to give degradation products. However, the methyl groups are meta to the amino function and should not yield a highly resonance-stabilized benzyl radical; in fact, reactivity little greater than that of toluene might be expected. Furthermore, the effect of acid could not be explained by reaction at the methyl groups, because protonation would reduce the reactivity of the triphenylmethane carbon-hydrogen bond to the same extent as the meta methyl group, and thus no change in chemistry would be expected.

Assuming that 0.036 sec is the normal "unhindered" rate of disproportionation of unprotonated 4600-Å species, it is seen that with the ortho methyl groups present in *o*-MLECV the rate is significantly slower (0.10 sec). In the normal "unhindered" reaction we know oxidation at the triphenyl methane carbon-hydrogen bond occurred since color is formed. In the hindered case reaction at some other point must occur since no color will form on acidification. A reasonable suggestion is either oxidation at the *N*-ethyl function or ring addition products. Reaction at the α -C-H bond of the *N*-ethyl group yields a relatively stable amidinium compound. Further reaction with solvent leads to ethers, etc. Acid or even chloride ion might interfere with

this reaction, since they tie up the nonbonding nitrogen electrons and make the α hydrogens less reactive. In this case the color forming reaction has time to occur.

To check to see if it is possible to bring about the destructive reaction with LECV by adding base to the solution, the photooxidation with lophine was carried out in the presence of methanolic sodium methoxide. Even 0.1 *M* alkoxide ion in methanol is not sufficient to interfere with the color reaction with LECV. This must mean that, even if the equilibrium



is completely to the right, the triphenylmethyl radicals will disproportionate with LECV to produce the cation. Using these same arguments for *o*-MLECV, it is interesting to speculate how an apparently small change in acidity can have a dramatic effect on both the rate and course of the disproportionation reaction. A tentative set of intermediates that explain these results are shown in Scheme I, p 2279.

Registry No.—L., 29897-74-3; L₂, 1707-68-2; *o*-MLECV, 4482-70-6; *o*-MLECV·3HCl, 4482-56-8; LECV, 4865-00-3.

Acknowledgments.—We wish to thank R. Dessauer, L. A. Cescon, G. R. Coraor, and C. Yembrick for developing our interest in this problem. We also thank V. F. Hanson for the flash photolysis apparatus and J. M. White for assistance in carrying out the experiments.

Substituent Effects on the Reactivity of Triarylimidazolyl Free Radicals toward Tris(2-methyl-4-diethylaminophenyl)methane

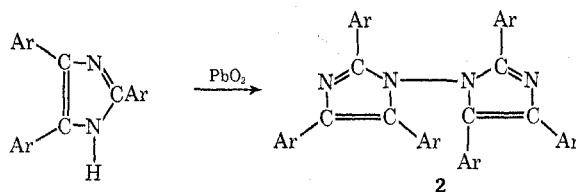
ROBERT L. COHEN

Contribution No. 448 from the Jackson Laboratory, Research and Development Division, Organic Chemicals Department, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

Received February 12, 1970

The effect of aryl substituents on the reactivity of substituted triarylimidazolyl free radicals, photolytically generated from their corresponding dimers, in an electron-exchange reaction with an aminotriphenylmethane substrate was studied by flash photolysis. The reaction rate was retarded by electron-donating substituents and enhanced by electron-withdrawing groups on the imidazolyl radical. Bulky substituents, ortho to the imidazole ring, also increased the reactivity. These results are consistent with the previously proposed mechanism for the reaction.

The preparation of 2,4,5-triphenylimidazole (lophine) was first reported in 1882.¹ In 1960, Hayashi and Maeda reported that oxidation of lophine **1** and its de-



rivatives yields dimeric products which are photo-, piezo-, and thermochromic due to the reversible formation of a colored 2,4,5-triarylimidazolyl free radical. They proposed a hydrazine-type structure **2** to account

for the dimer's properties.² The same structure was suggested by Zimmermann and coworkers³ who prepared a series of these compounds. On the basis of infrared spectral data, White and Sonnenberg⁴ proposed that the thermally unstable dimer originally formed in the oxidation of unsubstituted lophine is the 4,4' isomer **3** which isomerizes in solution to the thermally stable 1,2' dimer **4** through the intermediacy of the free radical **5**. The stable 1,2' isomer is the only dimer readily obtained on oxidation of lophines containing an

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