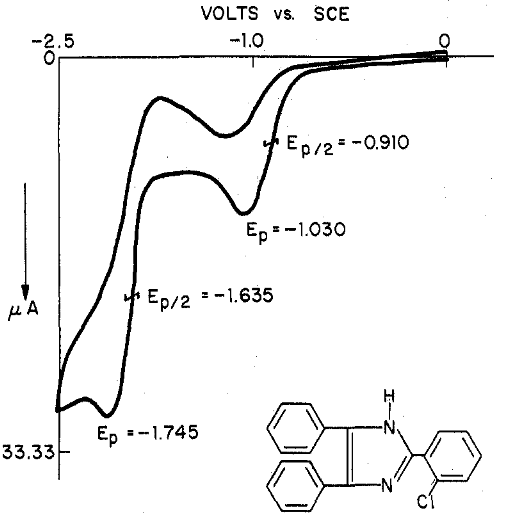

2-(2-chlorophenyl)-4,5-diphenylimidazole, 0.00130 *M*

Figure 5.—Cyclic voltammetry: temperature 25 ± 0.1°; electrode system Pt *vs.* sce; 0.5 *M* $LiClO_4$ in acetonitrile.

flux 3.5 hr. A precipitate, formed when the solution cooled, was crystallized from benzene to give 0.33 g of 2-(4-methoxyphenyl)-4,5-diphenylimidazole (**4c**), mp 230–232°, λ_{max} 297 mμ. From the remaining solid product was isolated 0.14 g of dark green quinhydrone **12**, mp 169–171°.

7. **With 2-(4-Methoxyphenyl)-4,5-diphenylimidazole (4c).**—A 25-ml benzene solution of 0.05 g of biimidazole **1a** and 0.05 g of **4c** was irradiated with a sun lamp to give a blue solution of radical **2c**, λ_{max} 610 mμ. Irradiation of a benzene solution of **4c** in the absence of biimidazole **1a** gave no radical which could be detected spectrally or by esr.

8. **With 1,2,2-Tricyanoethyl-*N*,*N*-dimethylaniline (13).**—A solution of 1:1 by volume acetone–benzene, containing 0.5% each of **13** and biimidazole **1b**, was irradiated with the sun lamp. The known orange 4-(1,2,2-tricyanovinyl)-*N*,*N*-dimethylaniline (**14**) was identified spectrally.[22]

9. **With 3-Methyl-2-benzothiazole Hydrazone Hydrochloride (15). Oxidative Coupling with *N*,*N*-Dimethylaniline Hydrochloride.**—A solution prepared in the dark of 0.635 g of **15**, 0.468 g of *N*,*N*-dimethylaniline hydrochloride, and 1.0 g of biimidazole **1b** was irradiated for 10 min with the sun lamp. The solution was diluted with 100 ml of water and extracted with three 50-ml portions of petroleum ether, which were discarded. The aqueous methanol solution was concentrated on a steam bath, cooled to room temperature, and filtered. The filtrate was saturated with sodium chloride and a blue-black crystalline solid formed. The uv and visible spectra (methanol) of this solid were identical with those of 3-methyl-2,4-(dimethylaminophenylazo)benzothiazolium chloride (**16**) prepared according to Hünig.[23]

10. **With Mercaptans. a. 1-Butanethiol.**—Under an atmosphere of dry nitrogen, a mixture of 2.7 g of butanethiol, 3.3 g of biimidazole **1b**, and 20 ml of benzene was heated with stirring. The refluxing solution was irradiated (through Pyrex glass) with the sun lamp, 2 in. distant for 20 hr. The mixture was cooled and precipitate formed. This solid, mp 193.0–194.5°, was identical in infrared spectrum with authentic 2-(2-chlorophenyl)-4,5-diphenylimidazole (**4b**). The filtrate was shown by comparison of its ir spectrum and gas chromatographic analysis with those of authentic material to contain a high concentration of dibutyl disulfide.

b. Thiophenol.—A similar reaction was carried out with 0.44 g of thiophenol and 1.2 g of biimidazole **1a** in 15 ml of benzene. Triphenylimidazole **4a**, mp 190.0–191.5°, formed as a precipitate, and the phenyl difulfide was identified, as above, in the filtrate.

Spectral Determinations.—A Cary Model 14 spectrophotometer was used for uv and visible measurements. A Perkin-Elmer Model 221 instrument was employed for the infrared.

Cyclic Voltammetry.—The cell-electrode system was flushed with dry nitrogen and thermostated at 25 ± 0.5°. Acetonitrile (25 ml), 0.5 *M* in $LiClO_4$, and the sample (0.001–0.005 mol) were further flushed 5 min. The potential was scanned cyclically between 0 and +2.0 V *vs.* sce at a scan rate experimentally varied between 1 and 2.5 V/min. The cell was blanketed under nitrogen and shielded from light during the reaction. A representative polarogram is shown in Figure 5.

Reversibility of electrolytic triarylimidazole ⇄ biimidazole redox reaction was demonstrated by (a) observing no hysteresis in repetitive cycling and (b) obtaining the same cyclic trace from the biimidazole as from the corresponding imidazole.

Registry No.—**7b**, 21356-01-4; **7d**, 29920-21-6; **12**, 106-34-3.

Acknowledgment.—We are grateful to Drs. B. C. McKusick and R. Cohen for supplying samples, and to Dr. C. E. Looney for valuable discussions.

---

[22] B. C. McKusick, R. E. Heckert, T. L. Cairns, D. D. Coffman, and F. W. Mower, *J. Amer. Chem. Soc.*, **80**, 2806 (1958).

[23] S. Hünig and K. H. Fritsch, *Justus Liebigs Ann. Chem.*, **609**, 143 (1957).

The Flash Photolysis of a Substituted Hexaarylbiimidazole and Reactions of the Imidazolyl Radical

R. H. RIEM, A. MACLACHLAN, G. R. CORAOR,* AND E. J. URBAN

Contribution No. 459 from the Organic Chemicals Department and Contribution No. 1582 from the Central Research Department, E. I. du Pont de Nemours and Company, Experimental Station, Wilmington, Delaware 19898

Received February 12, 1970

The rate of reaction of 2-(*o*-chlorophenyl)-4,5-diphenylimidazolyl radicals (L·) with additives has been studied in various solvents. Evidence based on measured rate constants, including kinetic deuterium isotope effects, prove that the rate-determining step in the reaction L· + aromatic amine is an electron exchange reaction at the amino nitrogen, while in the reaction L· + hydroquinone the rate-determining step is hydrogen abstraction.

Lophine dimer [(bis(2,4,5-triphenylimidazole)] has been known and studied for many years. It was first prepared in 1960[1] although at the time the structure was incompletely characterized. The first clearly recognized synthesis[2] was published the following year. The observed photochromism[1] of the hexaarylbiimidazole was subsequently shown to be due to the formation of imidazolyl radicals[3,4] upon photodissociation of the parent compound. In the present study, the kinetics and mechanism of reactions of 2-(*o*-chlorophenyl)-4,5-diphenylimidazolyl radicals (L·) with aromatic

---

[1] T. Hayashi and K. Maeda, *Bull. Chem. Soc. Jap.*, **33**, 565 (1960).

[2] H. Zimmermann, H. Baumgärtel, and F. Bakke, *Angew. Chem.*, **73**, 808 (1961).

[3] H. Baumgärtel and H. Zimmermann, *Z. Naturforsch.*, *B*, **18**, 406 (1963).

[4] T. Hayashi, K. Maeda, and M. Takeuchi, *Bull. Chem. Soc. Jap.*, **37**, 1717 (1964).

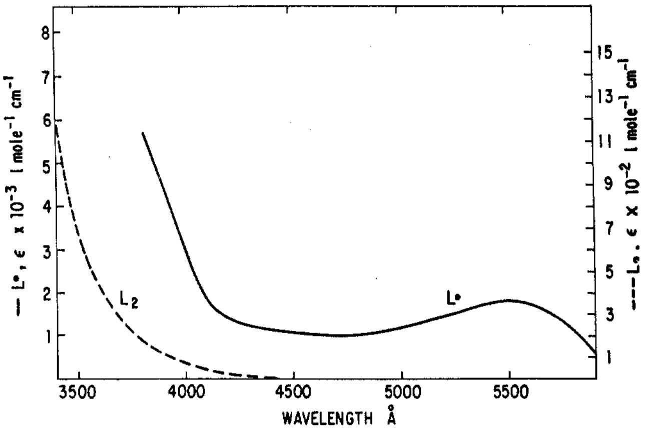

Figure 1.—Spectrum of L_2 (- - -) in CH_3OH; spectrum of L·(—) in EPA at −196°.

amines and with hydroquinone are studied in detail. The absence of thermal dissociation of the parent biimidazole at room temperature dictated the selection of this particular compound.[5]

Experimental Section

All compounds, except solvents, used in this study were prepared and supplied as described in ref 5. Solvents were the highest purity grades commercially available and were used directly. Linde high-purity dry (99.996%) argon was used in deoxygenating the solution in all flash-photolysis experiments. Spectra were recorded on Model 14 and Model 15 Cary spectrophotometers.

The flash-photolysis apparatus was of conventional design;[6,7] 160 *J* per flash were discharged through a PEK Laboratory XE 1-3 flash lamp placed parallel to the long axis of a 1-cm-diameter, 4-cm-long quartz cell. The flash was filtered with a combination 0-52 plus 7-60 Corning filter to provide light of 3700 ± 200 Å. The width of the flash intensity at half-peak height was 4.8 μsec. The appropriately filtered high-intensity analysis light was focused on the input slits of a Bausch and Lomb monochromator. A Dumont 6292 photomultiplier was used in conjunction with a Tektronic oscilloscope to monitor the transient absorptions.

Results and Discussions

Spectra.—The spectrum of 2,2 -bis(*o*-chlorophenyl)-4,4',5,5'-tetraphenylbiimidazole (L_2) in CH_3OH is given in Figure 1. The spectrum of L· (Figure 1) was obtained by photolysis of L_2 in EPA at −196°. The time involved in recording the L· spectrum was shown to be short compared to the rate of L· disappearance at the temperature employed. The method used to determine the extinction coefficient of L· at 5480 Å is described below. This spectrum is also identical with that taken point by point at room temperature using the flash-photolysis apparatus. A plot of the integrated flash intensity *vs.* the optical density change (OD) due to L· formation is a straight line (Figure 2). The small intercept in Figure 2 is due to experimental inaccuracies. The decay of L· was measured by flash photolysis at 25° in various deoxygenated solvents. This decay, which was followed at 3900 and at 5450 Å, was found to be slow and to follow second-order kinetics. A typical second-order plot obtained is given in Figure 3. In view of the photochromic behavior of the hexaarylbiimidazoles, the observed decay is interpreted as

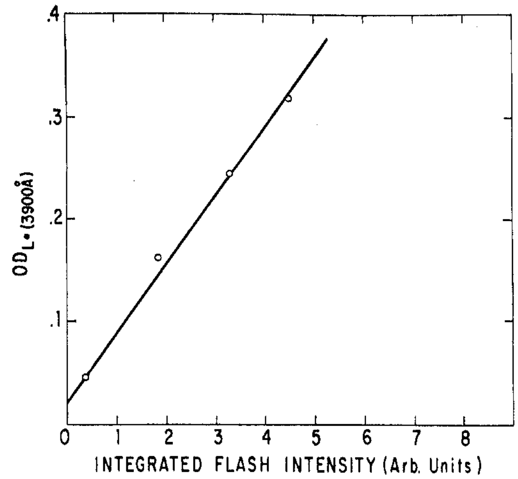

Figure 2.—The integrated flash intensity *vs.* the optical density of L·, both observed at 3900 Å.

$$2\mathrm{L}\cdot \xrightarrow{k_1} \mathrm{L}_2 \qquad (1)$$

Reactivity of L· with Aromatic Amine.—The flash photolysis of L_2 in the presence of various aromatic amines was investigated. Adequate amine was incorporated to yield pseudo-first-order kinetics as shown by variation of the amine concentration. The rate constants are listed in Table I.

Table I

Flash Photolysis of L_2 (2×10^{-4} *M*) at 25° in CH_3OH in the Presence of Amines

No.	Compd	k_4,[a] l. M^{-1} sec^{-1}	k'_4,[b] l. M^{-1} sec^{-1}
1	*N,N*-Diethylaniline		4.4×10^4
2	*N,N*-Dimethyl-*p*-toluidine		1.6×10^6
3	*N,N,N',N'*-Tetramethyl-*p*-phenylenediamine	7.0×10^7	3.5×10^7
4	Tris(*p*-diethylaminophenyl)-methane (leuco ethyl crystal violet)	1.2×10^7	4.0×10^6
5	Tris(*p*-diethylamino-*o*-methylphenyl)methane	2.5×10^7	8.3×10^6
6	Pyridine	No reaction	
7	2,6-Lutidine	No reaction	
8	*p*-Cyano-*N,N*-diethylaniline		3.74×10^2
9	*p*-Methoxy-*N,N*-diethylaniline		1.0×10^7
10	*p*-Chloro-*N,N*-diethylaniline		3.8×10^3

[a] k_4 is the overall second-order rate constant for L· reaction with the aromatic amine. k'_4 was calculated from the experimentally determined pseudo-first-order rate constant and the concentration of amine. k_4 was calculated on the basis of the "amino group concentration" and is equivalent to k'_4/number of amino functions per molecule of amine. [b] k'_4 is the rate constant calculated on the basis of amino group concentration.

If the point of attack of L· on the leuco triphenylmethane dyes no. 4 and 5 of Table I is considered to be the hydrogen atom attached to the central C atom, it is difficult to imagine how in the more sterically hindered case (no. 5) the rate constant could be double that found with compound no. 4. The gen-

---

(5) L. A. Cescon, G. R. Coraor, R. Dessauer, A. S. Deutsch, H. L. Jackson, A. MacLachlan, K. Marcali, E. M. Potrafke, R. E. Reed, E. F. Silversmith, and E. J. Urban, *J. Org. Chem.*, 2267 (1971).

(6) E. J. Land and G. Porter, *Trans. Faraday Soc.*, **59**, 2027 (1963).

(7) A. MacLachlan, *J. Phys. Chem.*, **71**, 718 (1967).

TABLE II

DEUTERIUM ISOTOPE EFFECT AT 25° DEOXYGENATED SOLUTIONS[a]

No.	Compd	Solvent	Rate constant for attack of L·, l./(mol sec)	Isotope effects, k_H/k_D
1	Hydroquinone (H_2Q)	H_2O saturated benzene	2.16×10^7	5.6/1
2	Hydroquinone (D_2Q)	D_2O saturated benzene	$3.86 + 10^6$	
3	Hydroquinone (H_2Q)	CH_3CN + 0.8% H_2O	2.68×10^6	10/1
4	Hydroquinone (D_2Q)	CH_3CN + 08% D_2O	2.6×10^5	
5	Hydroquinone (H_2Q)	CH_3CN + various H_2O amounts	2.7×10^6	
6	Tris(*p*-diethylamino-*o*-methylphenyl)methane	CH_3CN + 0.8% H_2O	1.07×10^4	1/1
7	Tris(*p*-diethylamino-*o*-methylphenyl)-methane	CH_3CN-0.8% H_2O	0.99×10^4	

[a] $L_2 = 4 \times 10^{-4}$ *M*, hydroquinone $= 2 \times 10^{-4}$ *M*, tris(*p*-diethylamino-*o*-methylphenyl)methane $= 10^{-4}$ *M*.

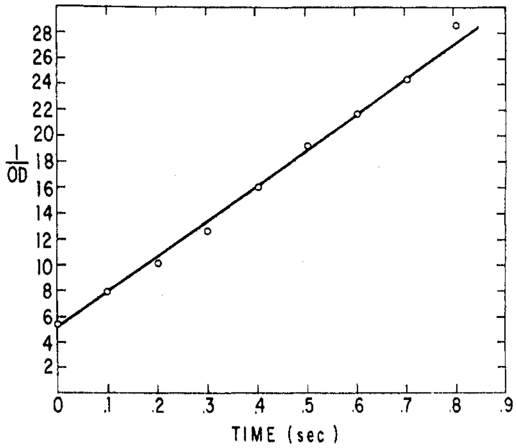

Figure 3.—Second-order plot obtained for the L· decay in CH_3OH measured at 5450 Å.

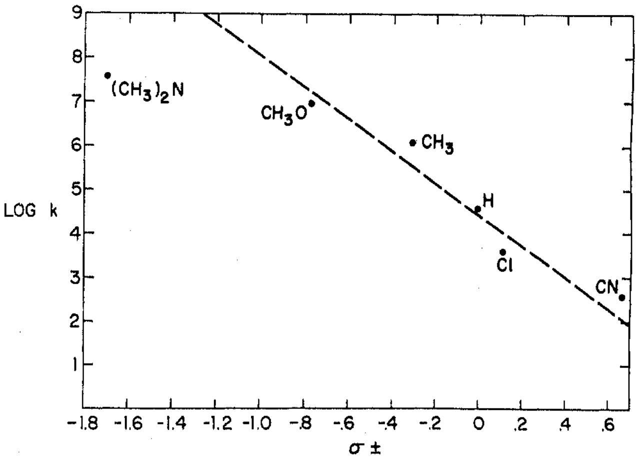

Figure 4.—Hammett plot of lophine radical reactivity with para-substituted *N,N*-diethylaniline. The dimethylamino substituent was done with *N,N,N',N'*-tetramethyl-*p*-phenylenediamine.

eral trend in Table I indicates that the reaction of L· with the amines listed occurs at the nitrogen atom. Substitutions which increase the electron density at this atom increase k_4. The reaction, therefore, is formulated as an electron-exchange reaction.

$$L\cdot + >\ddot{N}- \longrightarrow L^- + >\underset{+}{\dot{N}}- \qquad (2)$$

Additional evidence for the involvement of the free electron on the nitrogen can be obtained from the Hammett plot of para-substituted *N,N*-diethylaniline derivatives in Figure 4. A fairly good straight line is obtained with σ ± values, which suggests strong resonance interaction during the electron-exchange reaction. For information, the rate for *p-N,N*-dimethylamino is included in the plot. Nitrogen-positive radical ions of the type shown in eq 2 have been observed in the CCl_4-sensitized oxidation of leuco ethyl crystal violet.[7]

Reactivity of L· with Phenols.—Deuterium isotope effects were measured by flash photolysis in the reaction of L· with amines and hydroquinone. The hydroquinone reaction was studied to establish whether hydrogen abstraction or electron exchange is rate determining for phenol type structures, as it must be for the aromatic amines examined. The results are listed in Table II.

The data in Table II clearly demonstrate that in the reaction

$$L\cdot + \text{hydroquinone} \longrightarrow$$

hydrogen abstraction is the rate-determining step and support the concept of electron exchange (eq 2) in aromatic amine + L· reactions by showing the isotope effect is not related to deuteration of the L· radical. The dual mode of reactions by lophine radicals is interesting and it remains for further experimentation to establish if a phenol structure can be highly substituted enough to change the mode of reaction from hydrogen abstraction to electron exchange. The solvent effect on the magnitude of the isotope effect is also interesting. The solvating nature of the aqueous acetonitrile slows the overall reaction rate down by a factor of approximately ten and at the same time gives a much greater isotope effect. The slower reaction in acetonitrile suggests that a strong interaction between L· and substrate is involved which, if tempered by outside solvating, is rendered less efficient. The much larger isotope effect is consistent with the picture.

Registry No.—L·, 29897-74-3; L_2, 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

A. MacLachlan* and R. H. Riem

Contribution No. 1580 from the Central Research Department, E. I. du Pont de Nemours and Company, Experimental Station, Wilmington, Delaware 19898

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 Lewis[4-7] and Linschitz[8,9] and a previous publication[10] 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 series[11] discussed the reactions of the 2-(*o*-chlorophenyl)-4,5-triphenylimidazolyl radicals (L·), formed from the corresponding dimer (L_2), 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 L_2 were prepared by Cescon.[11a] The solvent CH_3OH 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 appratus designed by Dr. D. C. Reitz. The methanol solution containing leuco dye and CCl_4 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 L_2 in Various Solutions.—Ultraviolet absorption spectra of the *o*-MLECV·3HCl + L_2 mixture in methanol revealed no complexing between initiator and leuco dye. (Unless specified otherwise, all work was performed with *o*-MLECV at $6.6 \times 10^{-5}\ M$ and L_2 at $4 \times 10^{-4}\ M$.) The equilibrium constant K at 25° for the reaction

$$o\text{-MLECV}\cdot 3(\mathrm{H^+Cl^-}) \rightleftharpoons o\text{-MLECV}\cdot 2(\mathrm{H^+Cl^-}) + \mathrm{H^+} + \mathrm{Cl^-} \rightleftharpoons \text{etc.}$$

was determined in methanol, glycerol, acetonitrile, and dimethylformamide (Table I). These values were obtained by comparing the extinction coefficient at 2650 Å of *o*-MLECV·3HC1 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

Table I

Degree of Protonation at 25°[a]

$$\mathrm{DH\cdot 3HCl} \rightleftharpoons \mathrm{DH\cdot 2HCl} + \mathrm{HCl} \rightleftharpoons \text{etc.}$$

	k, 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	$\sim 10^{-7}$	DH·2.9HCl

[a] DH·3HCl = $6.6 \times 10^{-5}\ M$ and $L_2 = 4 \times 10^{-4}\ M$.

---

(1) C. A. Parker, Photochem. *Liquid Solid States, Pap. Symp.*, 38 (1957).

(2) S. Matsumoto, *Bull. Chem. Soc. Jap.*, **37**, 491 (1964).

(3) M. Kazumi, S. Kato, Y. Usui, S. Hayashi, and M. Morita, International Symposium of Photochemistry, Rochester, N. Y., 1963, Report AD 436086.

(4) G. N. Lewis, D. Lipkin, and T. T. Magel, *J. Amer. Chem. Soc.*, **63**, 3005 (1941).

(5) G. N. Lewis and M. Kasha, *ibid.*, **66**, 2100 (1944).

(6) G. N. Lewis and D. Lipkin, *ibid.*, **64**, 2801 (1942).

(7) G. N. Lewis and J. Bigeleisen, *ibid.*, **65**, 2414 (1963).

(8) (a) H. Linschitz, M. L. Berry, and D. Schweitzer, *ibid.*, **76**, 5833 (1954); (b) J. Eloranta and H. Linschitz, *J. Chem. Phys.*, **38**, 2214 (1963).

(9) H. Linschitz, J. Rennert, and T. M. Korn, *J. Amer. Chem. Soc.*, **76**, 5839 (1954).

(10) A. MacLachlan, *J. Phys. Chem.*, 718 (1967).

(11) (a) L. S. Cescon, G. R. Coraor, R. Dessauer, A. S. Deutsch, H. L. Jackson, A. MacLachlan, K. Marcali, E. M. Potrakfe, R. E. Read, E. F. Silversmith, and E. J. Urgan, *J. Org. Chem.*, **36**, 2267 (1971); (b) R. H. Riem, A. MacLachlan, G. R. Coraor, and E. J. Urban, *ibid.*, **36**, 2272 (1971).