The Molecular Oxygen Induced Chemiluminescence of Aryl Grignard Reagents

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Abstract: The molecular oxygen induced chemiluminescence of aryl Grignard reagents in diethyl ether and tetrahydrofuran solutions has been investigated. The main emitting species in the chemiluminescent reactions of phenylmagnesium bromide and p-chlorophenylmagnesium bromide have been identified as an isomeric mixture of brominated biphenyls identical with that formed through photolysis of the Grignard precursor. Possible mechanisms for the production of the excited biphenyls are discussed.

The molecular oxygen induced chemiluminescence of the ubiquitous Grignard reagent is a well-known, though little understood, phenomenon. This chemiluminescence was first reported by Wedekin in 1906[1] and investigations into the qualitative aspects of this light emission were undertaken during the 1920's. These investigations showed that the magnesium bromides exhibit the brightest chemiluminescence and that substituents enhance the chemiluminescence in the order chloro > methyl > bromo > iodo, with para substituents being much more effective than ortho and meta in enhancing the chemiluminescence.[2,3] Application of a magnetic field (15 kG) was found to enhance the intensity of the chemiluminescence and during the electrolysis of phenylmagnesium bromide light emission occurs at the anode.[4] This early work is reviewed in Kharasch and Reinmuth's monumental treatise[5] and in two recent review articles.[6,7] Since about 1930 there has been seemingly little interest in this phenomenon, there being only two modern investigations.[8,9]

A number of factors interested us in this chemiluminescent reaction. The oxygen induced chemiluminescence of p-chlorophenylmagnesium bromide, for example, is so bright that it may be used as a lecture room demonstration.[10] This high intensity would allow determination of the chemiluminescence spectrum without elaborate experimental apparatus. Also, since there have been many investigations into the reaction of Grignard reagents with oxygen in the past decade[11-14] we had access to much information not available to previous investigators. Lastly, chemiluminescence is in general a well known, though little understood, phenomenon. Previous studies of chemiluminescent reactions have shown, however, that such investigations can often lead to information concerning a wide range of chemical problems.

In this investigation the main emitters in the chemiluminescent reactions of phenylmagnesium bromide and p-chlorophenylmagnesium bromide have been identified as brominated biphenyls. The fluorescence spectra of the brominated biphenyls were found to be a good match to the chemiluminescence spectra, as shown in Figures 1 and 2. The isomeric distribution of the brominated biphenyls is the same as that produced through the known radical pathway of photolysis.[15] Based on these and other data, some plausible mechanisms can be written.

Experimental Section

Preparation and Assay of Grignard Reagents. Phenylmagnesium bromide and p-chlorophenylmagnesium bromide were prepared in the usual manner under nitrogen with a 50% excess of magnesium. Mallinckrodt anhydrous diethyl ether, tetrahydrofuran (THF), and bromobenzene and 1-bromo-4-chlorobenzene (Matheson Coleman and Bell) were used without further purification. Baker and Adamson Grignard grade magnesium and doubly distilled magnesium (a gift from Dr. Harry Johnson) were heated to 120° before use to remove traces of water. The Grignard reagents were usually prepared at 0.1 M concentration. The samples for the epr studies discussed below were prepared at 1 M. A Varian A-60D nmr spectrometer was used to determine the concentration of the Grignard reagents and these were within 5% of those determined by Gilman's acid titration method.[16] Diphenylmagnesium was prepared free of halogen from diphenylmercury (Alfa Inorganics) which was reacted with an excess of doubly distilled magnesium in diethyl ether or THF.

Preparation and Assay of Oxidation Products and Brominated Biphenyls. The Grignard reagents were oxidized by a stream of dry commercial oxygen which was bubbled through the constantly stirred solution for about 2 hr. Thin-layer chromatograms (tlc) of the oxidation products using standard procedures for n-hexane, chloroform, benzene, and cyclohexane on Merck AG F 254 silica gel showed one fluorescent spot for the oxidation products of phenylmagnesium bromide and a broadened spot for the oxidation products of p-chlorophenylmagnesium bromide. The R_f values for the fluorescent material was about 0.8 when benzene was used as eluent. Exposure of the tlc plates to iodine showed the existence of a large number of nonfluorescent spots in both cases.

Brominated biphenyls were formed through the attack of phenyl radicals on the Grignard precursor. Phenyl radicals were formed

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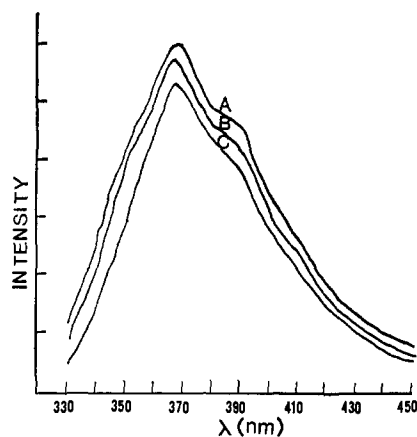
Figure 1. Fluorescence spectrum of oxygenation products of phenylmagnesium bromide in diethyl ether; wavelength of excitation. 313 nm (A); fluorescence spectrum of photolyzed bromobenzene in diethyl ether; wavelength of excitation, 313 nm (B); chemiluminescence spectrum of the reaction of a diethyl ether solution of phenylmagnesium bromide with oxygen (C).

Figure 2. Fluorescence spectrum of oxygenation products of p-chlorophenylmagnesium bromide in diethyl ether, wavelength of excitation, 313 nm (A); fluorescence spectrum of photolyzed 1-bromo-4-chlorobenzene in diethyl ether solution, wavelength of excitation. 313 nm (B); chemiluminescence spectrum of the reaction of a diethyl ether solution of phenylmagnesium bromide with oxygen (C).
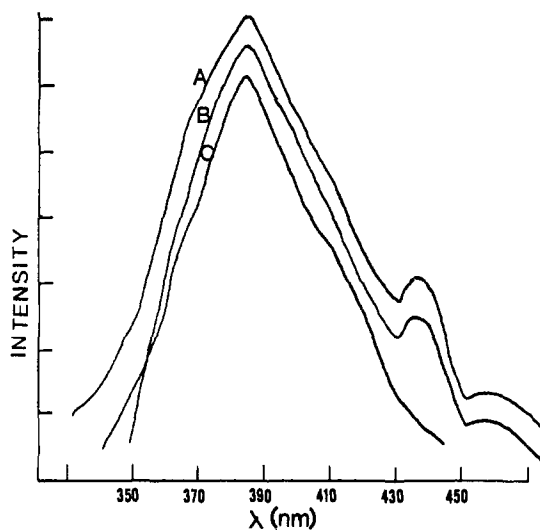
either by photolysis of bromobenzene[15] for 30 min by a low-pressure mercury lamp (primary radiation 253.7 nm, Rayonett photochemical reactor) or by the decomposition of benzoyl peroxide in bromobenzene at 80°.[17] The brominated biphenyls produced by these two methods gave rise to identical fluorescence spectra. The brominated biphenyls from 1-bromo 4-chlorobenzene were also formed by photolysis as above. All the solutions of brominated biphenyls exhibited a light brown color.

Spectroscopic Measurements. Fluorescence spectra of the Grignard oxidation products and the brominated biphenyls were obtained using right angle excitation with the 313- and 366-nm lines of a high-pressure mercury lamp. The fluorescence was monitored through a McPherson Model 2051 monochromator by an RCA 7625 photomultiplier and read out on a strip recorder. Fluorescence spectra were not corrected for monochromator or photomultiplier sensitivity. The fluorescence spectrum of the oxygenation products of p-chlorophenylmagnesium bromide was shown to consist of two components. The 366-nm mercury line excited only the long wave-

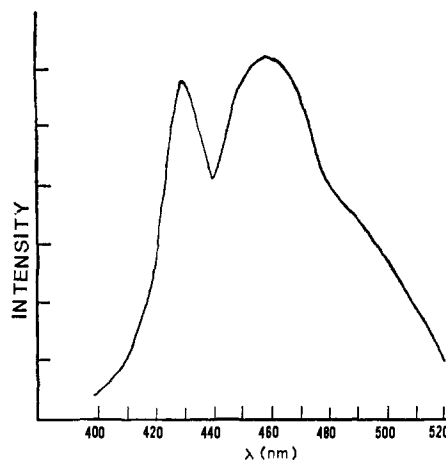(17) D. R. Augood, J. I. Cadogan, D. H. Hey, and G. H. Williams, J. Chem. Soc., 3412 (1953).

Figure 3. Fluorescence spectrum of oxygenation products of p-chlorophenylmagnesium bromide in diethyl ether; wavelength of excitation, 366 nm.

length component whereas the 313-nm line excited both the long and short wavelength components, as shown in Figures 2 and 3.

Chemiluminescence spectra were obtained by reacting a continuous constant flow of Grignard reagent with a stream of dry commercial oxygen. The Grignard solution was placed in a 250-ml reservoir and was gravity flowed into a 0.5 cm² cell. The flow rate was such that the Grignard solution was only partially oxidized after flowing through the cell. A stream of oxygen was introduced through a side arm in the cell. The pressure of the stream of oxygen was regulated to a critical value, about 4 psi, such that it was just sufficient to blow a thin layer of Grignard solution against the face of the cell on which the collecting optics were focused. The advantage of this method is that it minimizes self-absorption by the solution while the chemiluminescent intensity is kept high. Chemiluminescence spectra were reproducible whether the spectra were taken from longer to shorter wavelength or vice versa. Hence, the system delivered an approximately constant flow rate. The chemiluminescence was focused onto the slits of the McPherson monochromator-RCA photomultiplier system used in obtaining the fluorescence spectra. The chemiluminescence spectra were not corrected for monochromator or photomultiplier response. Grignard reagents prepared from doubly distilled magnesium exhibited the same chemiluminescence spectra and intensity as those prepared from Grignard grade magnesium. The oxygen induced chemiluminescence of phenylmagnesium bromide and p-chlorophenylmagnesium bromide is shown in Figures 1 and 2. These spectra are in good agreement with those previously obtained for triethylamine–benzene solutions of the Grignard reagents.[8]

Epr Spectroscopy. Epr spectra were taken on a Varian V-4052 epr spectrometer using an X-band bridge and a 0.15-mm quartz flat cell. No epr signal could be detected from a sealed 1 M sample of phenylmagnesium bromide in diethyl ether, but when the sample was exposed to atmospheric oxygen a weak epr signal ($g = 2$) could be detected. The epr signal was too weak to allow the observance of splittings and hence to identify the radical species. THF solutions of phenylmagnesium bromide exhibit the same behavior though the radical signal is weaker than in diethyl ether by a factor of about 2. No epr signal could be detected from oxygenated samples of p-chlorophenylmagnesium bromide, and this may be due to the fact that these solutions form a surface film when exposed to oxygen.

Results and Discussion

The chemiluminescence arising from the reaction of molecular oxygen with aryl Grignard reagents is one of the most energetic known. The chemiluminescence spectra shown in Figures 1 and 2 demonstrate that there is emission at wavelengths as short as 330 nm, corresponding to about 90 kcal. The chemiluminescent reaction must therefore supply at least this amount of energy. This energetic criterion eliminates all but a few possible reaction mechanisms from consideration. Furthermore, the chemiluminescence associated with

the reaction of aryl Grignard reagents and oxygen has been shown to be enhanced in the presence of a magnetic field[4] suggesting that radicals may be important in the chemiluminescent reaction.[18] Recently, Garst, et al.,[11] examined the oxygenation of phenylmagnesium bromide and on the basis of product distributions argued for the presence of radical intermediates. Our epr measurements on the oxygenation of phenylmagnesium bromide provide the first direct evidence for the formation of radicals during the reaction. This evidence leads us to consider radicals as important species in the generation of the light emission.

The chemiluminescence spectra shown in Figure 1 demonstrate that the chemiluminescence spectrum of phenylmagnesium bromide matches well the fluorescence spectrum of the oxygenation products and the fluorescence spectrum of the isomeric distribution of brominated biphenyls produced through the photolysis of bromobenzene. The chemiluminescence spectrum of the reaction of p-chlorophenylmagnesium bromide with oxygen was found to be a good match to the fluorescence of the oxygenation products of p-chlorophenylmagnesium bromide as the results in Figure 2 demonstrate. The fluorescence spectrum of the brominated biphenyls formed through the photolysis of 1-bromo-4-chlorobenzene is a good match to the chemiluminescence in the short wavelength region, as shown in Figure 2. When the long wavelength fluorescence of the oxygenation products is added to th fluorescence of the brominated biphenyls the resultant spectrum is a good match to the entire chemiluminescence spectrum. The compound(s) responsible for the long wavelength portion of the luminescence could not be identified. It is on the basis of the above spectral evidence that the brominated biphenyls are identified as the emitters in the chemiluminescent reaction.

In a previous investigation[8] of this chemiluminescence it was suggested that p-terphenyl is the emitting species. This assignment of p-terphenyl as the emitting species was based on a comparison of the chemiluminescence spectrum of the oxygenation of phenylmagnesium bromide and the fluorescence spectrum of p-terphenyl. However, the fluorescence spectrum of p-terphenyl that was used for comparison is incorrect. The true fluorescence spectrum of p-terphenyl[19] is not comparable to that published by Bardsley and Hercules,[8] and therefore their assignment is questionable.

There is a marked variation of the chemiluminescence intensity with solvent. In diethyl ether solutions the intensity is about 100 times more intense than THF solutions. Although no quantitative measurements were made it appears that the higher intensity is simply due to the fact that the oxidation rate in diethyl ether solutions of the Grignard reagents is about an order of magnitude greater than in THF. Addition of a THF solution of diphenylmagnesium to a THF solution of phenylmagnesium bromide does not enhance the chemiluminescence intensity. Since the oxidation of diphenylmagnesium in both diethyl ether and THF solutions is not chemiluminescent, the possible role of diphenylmagnesium in the chemiluminescence is ruled out.

Although we have concluded that the brominated biphenyls are the emitting species, this does not necessarily mean they are the excited-state species initially formed in the reaction. In order to determine whether or not the brominated biphenyls are formed initially in their excited state or whether they are excited by energy transfer from some other species, various acceptors such as anthracene, 9,10-disubstituted anthracene, and chrysene were added to the Grignard solution before oxygenation. For example, 9,10-dichloroanthracene was added to a concentration as high as 10^{-2} M and no fluorescence was observed from this molecule. Since the final concentration of brominated biphenyl after complete oxygenation is only about 10^{-3} M, we conclude that energy transfer to the anthracene should have been at least 10 times more efficient. In the initial stages of the oxygenation reaction, the concentration of brominated biphenyls is even lower and under those conditions 10^{-2} M anthracene should have totally quenched the luminescence from the brominated biphenyls.
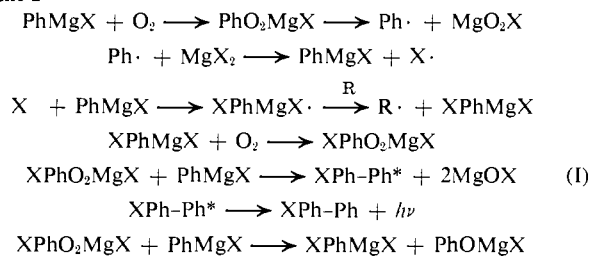
The sensitivity of the experimental technique was such that a decrease of 30% in the chemiluminescence intensity upon addition of acceptor could have been detected. If the fluorescence intensity of the acceptor was at least 10% of that of the chemiluminescence this would have been detected at the highest concentration of acceptor used (10^{-2} M 9,10-dichloroanthracene). In this case neither quenching of the chemiluminescence nor sensitized emission from the anthracene was observed. The nonappearance of sensitized emission from the anthracene is reasonable, even if the anthracene was receiving appreciable energy transfer, due to the highly efficient self-quenching of this molecule. The quenching of the excited brominated biphenyl by the anthracene at the concentration used would be appreciable, about 10–30%, depending on the lifetime of the excited brominated biphenyl and the diffusion coefficient of the anthracene in the Grignard solution. The amount of chemiluminescence quenching was at most 30%. Hence, it appears that the brominated biphenyls are formed in their excited state rather than being the recipients of energy transfer.

Unsubstituted biphenyl is also formed in the oxygenation of phenylmagnesium bromide in about 15% yield, depending on the reaction conditions, but no chemiluminescence is detected from the biphenyl. If the reaction forming biphenyl is assumed to be the same as that for the brominated biphenyls, then the energy supplied by the reaction is sufficient to excite one product but not the other. The difference in excitation energy between the substituted and unsubstituted biphenyl is not known, but a reasonable estimate, based on the energy difference between the maxima of the fluorescence spectra, is about 7 kcal. This alternative is satisfied by Scheme I.
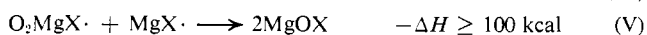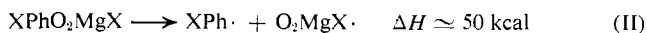
The energetics for the reaction giving rise to the excited biphenyl (eq I) can be estimated by breaking the reaction into ideal thermodynamic steps (eq II–V).[20]

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(20) The ΔH for eq II was estimated through analogy with the reaction $RO_2 \cdot \rightarrow R \cdot + O_2$: J. C. Calvert and J. N. Pitts, "Photochemistry," Wiley, New York, N. Y., 1964. The ΔH for eq III is not known and 70–90 kcal seems to be a reasonable estimate. The ΔH for eq IV was estimated from data in J. D. Roberts and M. C. Caserio, "Basic Principles of Organic Chemistry," W. A. Benjamin, New York, N. Y., 1965. The ΔH for eq V is not known and 100 kcal seems to be a reasonable estimate.
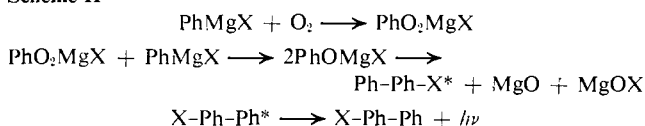
Scheme I

$$PhMgX + O_2 \longrightarrow PhO_2MgX \longrightarrow Ph\cdot + MgO_2X$$

$$Ph\cdot + MgX_2 \longrightarrow PhMgX + X\cdot$$

$$X\cdot + PhMgX \longrightarrow XPhMgX\cdot \xrightarrow{R} R\cdot + XPhMgX$$

$$XPhMgX + O_2 \longrightarrow XPhO_2MgX$$

$$XPhO_2MgX + PhMgX \longrightarrow XPh\text{-}Ph^* + 2MgOX \qquad (I)$$

$$XPh\text{-}Ph^* \longrightarrow XPh\text{-}Ph + h\nu$$

$$XPhO_2MgX + PhMgX \longrightarrow XPhMgX + PhOMgX$$

This gives an overall exothermicity of at least 100 kcal of which 90 kcal is necessary for exciting the brominated biphenyl.

$$XPhO_2MgX \longrightarrow XPh\cdot + O_2MgX\cdot \qquad \Delta H \simeq 50\ \text{kcal} \qquad (II)$$

$$PhMgX \longrightarrow Ph\cdot + MgX\cdot \qquad \Delta H \simeq 70\text{-}90\ \text{kcal} \qquad (III)$$

$$XPh\cdot + Ph\cdot \longrightarrow XPh\text{-}Ph \qquad -\Delta H \simeq 140\ \text{kcal} \qquad (IV)$$

$$O_2MgX\cdot + MgX\cdot \longrightarrow 2MgOX \qquad -\Delta H \geq 100\ \text{kcal} \qquad (V)$$

Alternatively, we could assume that the brominated biphenyls are formed through a different reaction path than the unsubstituted biphenyl. Such a reaction scheme is outlined in Scheme II. The energetics of this

Scheme II

$$PhMgX + O_2 \longrightarrow PhO_2MgX$$

$$PhO_2MgX + PhMgX \longrightarrow 2PhOMgX \longrightarrow$$

$$Ph\text{-}Ph\text{-}X^* + MgO + MgOX$$

$$X\text{-}Ph\text{-}Ph^* \longrightarrow X\text{-}Ph\text{-}Ph + h\nu$$

second alternative are basically the same as that of the first, but it is to be noted that the second alternative is not explicitly dependent on radical formation. In an effort to obtain information regarding the role of radicals in the chemiluminescence reaction we attempted to add radical quenchers to the Grignard solution before oxygenation. However, all the radical quenchers that we are aware of are unsatisfactory due either to insolubility or reaction with the Grignard reagent. A study of the magnetic field effect of the intensity of the chemiluminescence would be helpful in elucidating the role, if any, of radicals in the chemiluminescence.

Summary

The oxygen induced chemiluminescence of aryl Grignard reagents is a well-known though much neglected phenomenon. In this investigation the emitting species in the oxygenation of phenylmagnesium bromide and p-chlorophenylmagnesium bromide have been identified as the radical pathway isomeric distribution of brominated biphenyls. This conclusion was reached by comparing the chemiluminescence spectra, the fluorescence spectra of the oxygenation products, and the fluorescence spectra of brominated biphenyls formed through the photolysis of the Grignard precursor, as shown in Figures 1–3. An epr study showed that free radicals are formed during the oxygenation of phenylmagnesium bromide, but the full role of these radicals in the chemiluminescence could not be ascertained. To account for the chemiluminescence we proposed two reaction schemes, one of which depends explicitly on radical intermediates, and the other involves only nonradical species. Since the quantum yield of the chemiluminescence is quite low, at most 10^{-2}, these suggested mechanisms do not contradict the mechanism for the main reaction products proposed by Garst, et al.[11]

Elimination of Bisulfite Ion from a Series of Uracil–Bisulfite Adducts. Evidence for a Two-Step Mechanism[1]

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Abstract: Kinetic studies have been carried out on the elimination of bisulfite ion from the 5,6-dihydro-6-sulfonates of uracil, 1-methyluracil, 3-methyluracil, 1,3-dimethyluracil, and from the 5,5-dideuterio, cis-5-deuterio, and trans-5-deuterio analogs of 5,6-dihydrouracil-6-sulfonate. In the absence of significant concentrations of general acids, the reactions in aqueous solution were catalyzed by hydroxide ion and general bases and the 5,5-dideuterio and trans-5-deuterio derivatives were desulfonated less rapidly than their protio analogs. When larger concentrations of general acids were included in the reaction solution, the rates of desulfonation became less sensitive to the concentration of general bases and exchange of the trans deuterium atoms of the 5,5-dideuterio and trans-5-deuterio derivatives with protons from the solvent occurred more rapidly than desulfonation. These observations strongly suggest that elimination is occurring via a multi-step rather than a one-step mechanism as has previously been suggested.

Many reactions of uracil derivatives and related pyrimidines are now recognized to be initiated by covalent addition of a nucleophilic reagent across the $>C\text{-}6=C\text{-}5<$ bond of the pyrimidine molecule. Some