

LIGHT-INDUCED CHEMILUMINESCENCE IN DERIVATIVES OF COAL AND PETROLEUM

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INTRODUCTION

In connection with work requiring the use of a liquid scintillation spectrometer for the determination of radioactive methyl groups introduced into coal, we discovered that solutions of alkylated coal exhibited chemiluminescence when exposed to light in the presence of air. We subsequently found that solutions of other products derived from coal and petroleum also exhibited chemiluminescence. In this paper we report our observations and suggest a mechanism for this light-induced chemiluminescence in products derived from coal and petroleum.

EXPERIMENTAL

Materials Investigated — The materials investigated are described in table 1.

TABLE 1. - Materials Tested

<u>Material</u>	<u>Description</u>
Coal tar I	High temperature coal tar from Pocahontas No. 3 (lvb) coal prepared in 1% yield by Bm-AGA method. ^{a/}
Coal tar II	Commercial high temperature coal tar.
Coal asphaltenes	Obtained by combining samples from several coal hydrogenation runs carried out at Pittsburgh Coal Research Center.
Methylated coal Ethylated coal Butylated coal	Prepared by reductive alkylation of Pocahontas No. 3 (lvb) vitrain. ^{b/}
Petrolenes I	Pentane soluble portion of straight run residual asphalt (Venezuelean crude) 85/100.
Asphaltenes I	Pentane insoluble, benzene soluble portion (20%) of above asphalt.
Petrolenes II	Pentane soluble portion of straight run residual asphalt (Californian crude) 85/100.
Asphaltenes II	Pentane insoluble, benzene soluble portion (21%) of above asphalt.

^{a/} Technical Paper 685, U. S. Government Printing Office, Washington, D. C., 1946.

^{b/} H. W. Sternberg and C. L. Delle Donne, "Solvation and Reductive Alkylation of Coal via a Coal Anion Intermediate." Preprints of Papers presented at the Division of Fuel Chemistry, Atlantic City, N. J., September 8-13, 1968.

Apparatus — A tensor* lamp with a GE 1133 bulb (rated 32 candle power at 6 V. and 3.9 A.) was used as a light source and a liquid scintillation spectrometer, model 2101 by Packard Instruments Company was used to detect light emission. The quantum efficiency of the instrument was 16% at 3800 Å, 4% at 5500 Å, 1% at 6000 Å, and 0% at 6500 Å.

Procedure — One-tenth to 5 milligrams of the material dissolved in 20 ml. of toluene was placed in a 22 ml. counting vial provided with a screw cap. The vial was irradiated by a tensor lamp at a distance of 1 cm. between light bulb and wall of vial for a period of one minute. The vial was then placed in the cavity of the liquid scintillation spectrometer and counting was started 30 seconds after the irradiation had been completed. To obtain chemiluminescence decay curves, the intensity of light emission (in counts per 0.1 minute) was recorded at 30 second intervals.

RESULTS

Chemiluminescence Decay Rates — The count rate of a sample as determined by the liquid scintillation spectrometer is proportional to the intensity, I , of the emitted light. The decay of chemiluminescence intensity, I , with time was determined for the materials listed in table 1. In all cases straight line relationships were obtained when $I^{-1/2}$ was plotted vs. time. In all cases the straight line relationship held up to at least 85% completion. A typical chemiluminescence decay curve as obtained for butylated coal is shown in figure 1. The arrow marks 92% completion.

Spectral Region of Chemiluminescence — Qualitative information on the spectral region of the light emitted was obtained by wrapping the sample vial after irradiation in various Kodak Wratten Gelatin filters of known transmittance and recording the count rate. A zero count rate indicated complete absorption, a normal count rate no absorption. By this method we established that the light emitted during chemiluminescence was in the 4800-5200 Å region.

Wavelength of Irradiating Light — We were interested in determining whether irradiation with red light, i.e., light in the lower energy region of the visible spectrum is capable of inducing chemiluminescence. A solution of 10 mg. of Petrolenes I (see table 1) in 20 ml. toluene was irradiated for 1 minute with a red filter (transmission in the 6500 Å region) placed between tensor lamp and sample. The irradiated sample emitted light in the same spectral region as a sample irradiated with white light.

Intensity of Chemiluminescence — The chemiluminescence intensities of the various materials listed in table 1 were obtained by determining count rates after irradiation. The results are summarized in table 2.

The chemiluminescence of irradiated solutions can be detected by visual observation. A vial containing 20 mg. of petrolenes I in 20 ml. of toluene emits a greenish-blue light which is clearly visible to the dark-adapted eye. The intensity of the light emitted immediately after irradiation of this sample corresponded to about 10^6 counts per minute. The light remained visible for about 20 minutes after which time the count had dropped to approximately 2×10^4 counts per minute.

* Reference to a company or product name is made to facilitate understanding and does not imply endorsement by the U. S. Bureau of Mines.

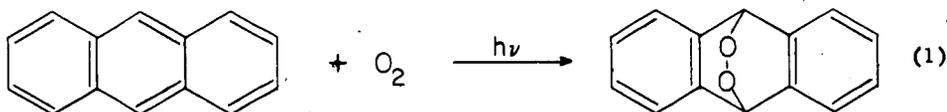
TABLE 2. - Intensity of chemiluminescence in products derived from coal and petroleum

<u>Material</u>	<u>Intensity, counts/min./mg.</u>	<u>Relative intensity</u>
Coal tar I	1.6×10^3	1.0
Coal tar II	6.2×10^3	3.9
Coal asphaltenes	7.1×10^4	4.4×10
Methylated coal	3.8×10^6	2.4×10^3
Ethylated coal	3.8×10^5	2.4×10^2
Butylated coal	2.0×10^5	1.3×10^2
Petrolenes I	7.9×10^3	4.9
Petroleum asphaltenes I	9.0×10^3	5.6
Petrolenes II	4.3×10^4	2.7×10
Petroleum asphaltenes II	6.5×10^4	4.1×10

DISCUSSION

We believe that the light-induced chemiluminescence we observed involves photo-sensitized addition of oxygen to acene-type ring systems to form labile endoperoxides followed by decomposition of these endoperoxides with emission of light. This view is consistent with the experimental evidence and is based on the following considerations.

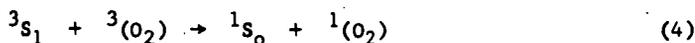
Moureau, Dufraisse and their co-workers^{1/} have shown that acene-type hydrocarbons such as anthracene react with oxygen under the influence of sunlight or artificial white light to form endoperoxides:



The mechanism^{2/} of this light-induced endoperoxide formation involves excitation of ground state triplet $\text{O}_2(^3\Sigma_g^-)$ to excited singlet $^1\text{O}_2(^1\Delta_g \text{ or } ^1\Sigma_g^+)$ by a sensitizer S. The sensitizer $^3\text{S}_0$ absorbs light energy to give an excited singlet state ($^1\text{S}_1$) which is converted by intersystem crossing to a triplet state



The sensitizer in its triplet state exchanges energy with triplet ground state oxygen to give singlet oxygen which adds to anthracene (A) to form the endoperoxide (AO_2):



Decomposition of the acene-type endoperoxides formed in coal and petroleum derived products with emission of light



explains the observed chemiluminescence. Rubrene endoperoxide, for example, decomposes at elevated temperature with emission of greenish-yellow light,³⁾ visible to the dark-adapted eye, to give oxygen and rubrene. On the basis of recent work^{4,5)} the emission of light observed during the decomposition of peroxides is attributed to transition of excited van der Waals type "double molecules" [$^1O_2 + ^1O_2$] to ground state oxygen 3O_2 . Depending on the state of the $(^1O_2)_2$ double molecule, light of different wavelengths can be emitted. The transition $(^1\Delta_g + ^1\Delta_g) \rightarrow 2\ ^3\Sigma_g^-$ produces light of 6335 Å (orange-red), $(^1\Delta_g + ^1\Sigma_g^+) \rightarrow 2\ ^3\Sigma_g^-$ light of 4780 Å (blue) and $(^1\Sigma_g^+ + ^1\Sigma_g^+) \rightarrow 2\ ^3\Sigma_g^-$ light of 3800 Å (ultraviolet) wavelength. The light observed in our experiments was in the 5000 Å region, corresponding to a $(^1\Delta_g + ^1\Sigma_g^+) \rightarrow 2\ ^3\Sigma_g^-$ transition.

The formation of an excited double molecule, $(^1O_2)_2$, resulting from the interaction of two endoperoxide molecules, AO_2



followed by rapid transition of $(^1O_2)_2$ to ground state with emission of light



is consistent with the observed decay rate, i.e., with a straight line relationship between $1/I^{1/2}$ and time. According to (6) and (7), the rate of light emission, I , is proportional to the $[AO_2]^2$ concentration and consequently $I^{1/2}$ may be substituted for the $[AO_2]$ concentration. In the integrated rate equation

$$1/c = 1/c_0 + kt \quad (6a)$$

the instantaneous concentration c is replaced by $I^{1/2}$ and the initial concentration by $I_0^{1/2}$. This leads to the observed straight line relationship between $1/I^{1/2}$ and time

$$1/I^{1/2} = 1/I_0^{1/2} + kt. \quad (6b)$$

According to equation (5), singlet oxygen (in either the $^1\Delta_g$ or $^1\Sigma_g^+$ state) is required for the formation of endoperoxide, a fact which determines the minimum of irradiating energy required to excite ground state triplet oxygen to excited singlet oxygen. The excitation energies for ground state oxygen ($^3\Sigma_g^-$) to singlet oxygen ($^1\Delta_g$) is 22.5 kcal (12,700 Å) and to singlet oxygen ($^1\Sigma_g^+$) is 37.5 kcal (7620 Å).⁸⁾ Consequently, light in the red region (44 kcal, 6500 Å), should contain sufficient energy for the excitation of ground state triplet to excited singlet oxygen, provided that sensitizers are present capable of absorbing this energy (equation 2) and of intersystem crossing (equation 3) to a triplet level whose energy lies above the energy (22.5 resp. 37.5 kcal) required for the 3O_2 to 1O_2 excitation. That sensitizers meeting these requirements are present in products derived from coal and petroleum follows from the observation that irradiating light in the red region (6500 Å) produces chemiluminescence in the blue-green (5000 Å) region. The formation of endoperoxide by irradiation in the presence of a sensitizer (methylene blue) absorbing in the red (6400 Å) region was recently demonstrated⁶⁾ in the case of rubrene. That singlet oxygen is involved in our light-induced chemiluminescence reaction is supported by the fact that addition of an excess of tetramethylethylene (TME) prior to irradiation reduces the chemiluminescence intensity by 98%. TME was shown to act as a captor for singlet oxygen and as an inhibitor in the photosensitized oxidation of rubrene.⁸⁾

Normal acene endoperoxides, containing a 9,10 bridge, are stable at room temperature, while the endoperoxides observed in coal and petroleum derivatives decompose with chemiluminescence at room temperature. This behavior is similar to that reported for the 1,4-endoperoxides formed by certain 1,4-dimethoxyanthracenes,^{7/} and suggests that the chemiluminescent endoperoxides in coal and petroleum derivatives are also of the 1,4 type and consequently contain activating substituents in the 1,4 positions. These substituents may be ethers present in the starting material, or in the case of alkylated coal, formed from OH groups during the alkylation. Moreover, the substituents undoubtedly need not be ethers, but probably could be any sufficiently electron-releasing groups, such as alkyl groups. This effect is illustrated by the 100-fold greater rate of formation of endoperoxide from 9,10-dimethylanthracene and singlet oxygen than from anthracene and singlet oxygen.^{8/} The activating effect of alkyl groups is undoubtedly the reason why alkylated coal exhibits chemiluminescence which is 2 to 3 orders of magnitude higher in intensity than that of the other materials examined (table 2).

CONCLUSIONS

Solutions of coal tar, coal asphaltene and alkylated coal as well as petroleum asphalt exhibit chemiluminescence when exposed to oxygen and light. This chemiluminescence is believed to be due to decomposition of endoperoxides formed by photooxidation of acene-type compounds present in products derived from coal and petroleum.

REFERENCES

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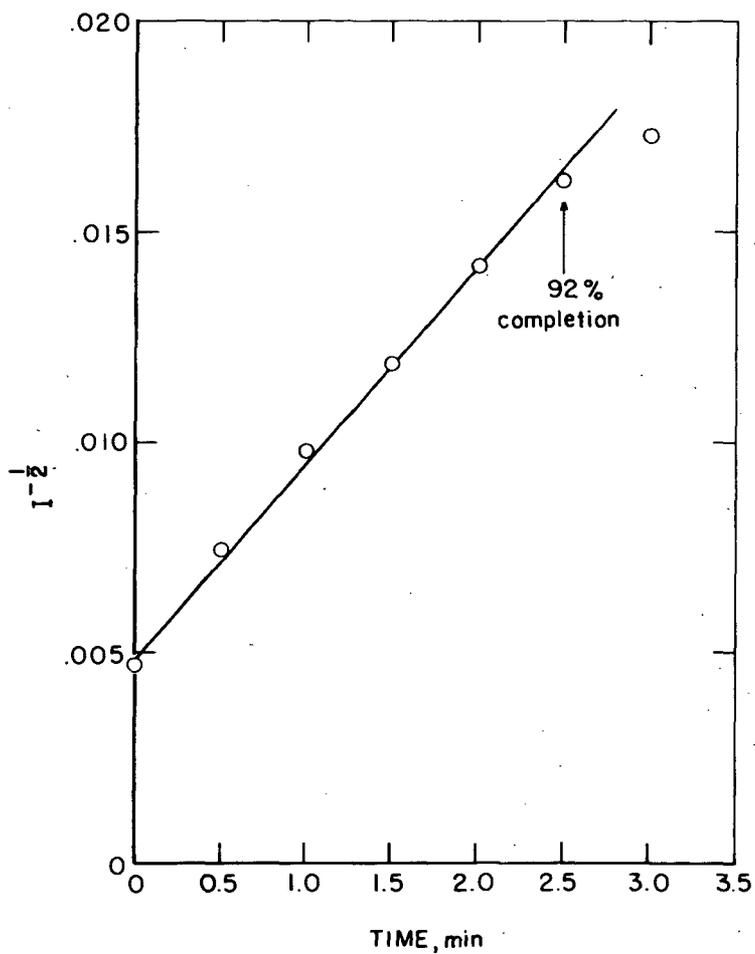


Figure 1- $I^{-\frac{1}{2}}$ vs time curve of chemiluminescence
decay for butylated coal.

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