Electrochemically Generated Chemiluminescence of Lucigenin[1]

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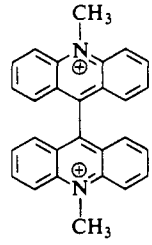
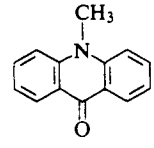
Abstract: The electrochemically generated chemiluminescence (ECL) of lucigenin has been studied in aqueous and nonaqueous systems. The electrochemical reduction of lucigenin has been shown to lead to dimethylbiacridene (DBA) as the product. The nonaqueous ECL has been shown to arise from reaction of superoxide with lucigenin. The spectral characteristics of the ECL, when compared with the fluorescence spectra and quantum efficiencies of NMA, DBA, and lucigenin, allow identification of the emitting species. NMA is the primary emitter formed in the excited state by the reaction of superoxide with lucigenin. In several systems a second longer wavelength component of emission was observed. This was the fluorescence of either DBA or lucigenin, depending on their respective concentrations and quantum efficiencies. Both DBA and lucigenin act as energy acceptors from excited NMA *via* singlet-singlet energy transfer. The experimental values of energy transfer rate constants (in the order of 1.5×10^{11} l./(mole sec)) correlate well with those derived from theoretical calculations.

The chemiluminescence (CL) of lucigenin (dimethylbiacridinium ion) (I) was first reported in 1935 by Gleu and Petsch.[3] They observed intense CL when lucigenin was treated with hydrogen peroxide in basic solutions. They also observed that this emission was either green or blue depending on the conditions under which the reaction was run. N-Methylacridone (II) was tentatively[4] and later conclusively[5] identified as the primary emitter in the blue CL reaction.



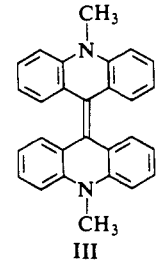
I



II

Since the discovery of this reaction, numerous studies have been carried out concerning its mechanism.[3-10] It has been shown that the reaction is of a redox type,[5,10] but the exact nature of the redox steps has not yet been ascertained. The electrochemical generation of lucigenin CL at a platinum electrode in basic aqueous solutions was reported by Tammamushi and Akiyama.[11] They observed light at the platinum electrode along the path of hydrogen evolution. No further work has been reported concerning the electrochemically generated CL (ECL) of lucigenin.

In the present study we have undertaken an electrochemical investigation of the lucigenin system in aqueous and nonaqueous solvents with emphasis placed on the electrochemical generation of lucigenin CL in nonaqueous solvents, a phenomenon heretofore not reported. The electrogeneration of superoxide from oxygen in relatively polar nonaqueous solvents, in the presence of lucigenin, causes production of light. Spectral studies of ECL, along with quantum yields of fluorescence and fluorescence spectra, have shown that N-methylacridone (NMA) is the primary emitter. A long-wavelength component is also observed in the ECL spectra and is assigned to either lucigenin or dimethylbiacridene (DBA) (III) fluorescence, depending on their respective concentrations and fluorescence efficiencies. Secondary emission has been shown to be due to singlet-singlet energy transfer from excited NMA to the appropriate acceptor.



III

Experimental Section

Reagents. Lucigenin (nitrate salt) was obtained from Columbia Organic Chemicals and was recrystallized twice from 50:50 methanol–ethanol before use. N-Methylacridone was obtained as a sample synthesized in the MIT Organic Laboratories[12] and was recrystallized from ethanol until a constant melting point of 202° was obtained. Dimethylbiacridene was prepared according to Decker and Petsch[13] and purified by recrystallization from chloroform.

Solvents. Absolute ethanol (EtOH) (U. S. Industrial Chemical Co.) was used as obtained. Dimethyl sulfoxide (DMSO), dimethylformamide (DMF) (Matheson Coleman and Bell, spectroscopic grade), and acetonitrile (AN) (Eastman Chemicals, spectroscopic grade) were dried over molecular sieves before use.

Apparatus. Electrochemical. The potentiostat used consisted of a Heath EUA-19-2 polarography module along with a Heath

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(2) National Institutes of Health Predoctoral Fellow, 1965–1968.
(3) K. Gleu and W. Petsch, *Angew. Chem.*, **48**, 57 (1935).
(4) A. Spruit-Van Der Burg, *Recueil*, **69**, 1525 (1950).
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(11) B. Tammamushi and H. Akiyama, *Trans. Faraday Soc.*, **35**, 491 (1939).
(12) We wish to thank Dr. D. Kemp for this sample.
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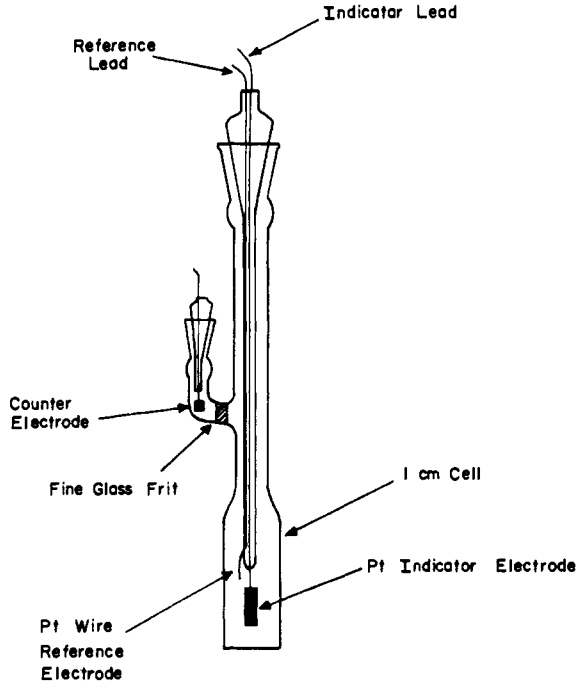

Figure 1. Electrochemical cell used for taking electrochemiluminescence spectra.

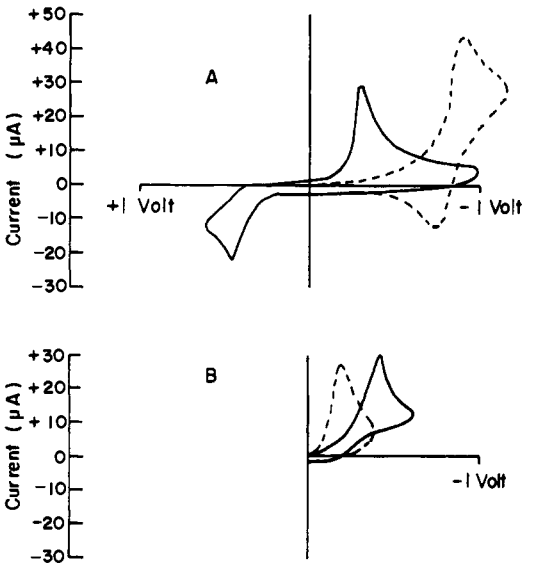

Figure 2. Current–voltage curves for lucigenin and oxygen. Curve A in DMSO at Pt electrode: solid line, lucigenin; dotted line, oxygen; supporting electrolyte 0.1 *M* tetrabutylammonium perchlorate; lucigenin concentration 1×10^{-3} *M*, oxygen-saturated solution. Curve B in H_2O at a Hg electrode: solid line, lucigenin, dotted line, oxygen; supporting electrolyte 0.1 *M* KCl. For both DMSO and H_2O, the reference electrode is Ag|AgCl in 0.1 *M* KCl, sweep rate 3 V/min.

EUW-14-A operational amplifier. In aqueous solutions 0.1 *M* KCl was used as the supporting electrolyte; in nonaqueous solutions 0.1 *M* tetrabutylammonium perchlorate was used. The reference electrode in all electrochemical measurements was Ag|AgCl in 0.1 *M* KCl. A platinum wire was used as the reference electrode in the ECL measurements.

Spectroscopic. Quantum efficiencies of fluorescence were obtained on a Turner Model 210 spectrofluorometer using 10^{-5} *M* quinine sulfate in 0.1 *M* H_2SO_4 as a standard. Lifetimes of fluorescence were obtained on a TRW Model 31A nanosecond fluorometry system. Fluorescence and ECL spectra were obtained on a system constructed from Aminco-Bowman spectrofluorometer building blocks and employing an EMI 9558 QA photomultiplier of S-20 response. Spectra are uncorrected.

Procedures. The electrochemical procedures were conventional. The coulometric measurements were done using a hydrogen–nitrogen gas coulometer described by Page and Lingane.[14] The technique for obtaining quantum yields of fluorescence has been reported by Turner.[15] The use of the TRW for lifetime measurements is described in their handbook.[16] ECL spectra were obtained by using the Aminco-Bowman spectrofluorometer with the electrochemical cell, shown in Figure 1, inserted in the cell holder.

Results and Discussion

Electrochemistry. Electrochemical studies were done in both aqueous and nonaqueous media. Typical cyclic-voltammetric curves for lucigenin and oxygen in DMSO at a platinum electrode (curve A) and in water at a mercury electrode (curve B) are shown in Figure 2. The solid line in curve A is the curve obtained with only lucigenin present in the solution. The wave peaking at −0.30 V corresponds to the reduction of lucigenin, and that peaking at +0.45 V corresponds to the oxidation of lucigenin's reduction product. The dotted line in curve A is the curve obtained with only oxygen present in the solution. The wave peaking at −0.9 V is the reduction of oxygen to superoxide, and that peaking at −0.85 V is the reoxidation of superoxide to oxygen. The reduction of lucigenin is irreversible, and in aqueous solutions the reduction product was insoluble and plated out on the electrode. There is a definite relationship between the lucigenin reduction wave and the oxidation wave of its reduction product. The peak at +0.45 V was observed only after first sweeping over the lucigenin reduction. If the initial sweep was anodic, no peak was observed at +0.45 V. The reduction product was isolated and identified as being DBA (III) by its infrared, uv, and mass spectra. With only DBA present, an oxidation peak was observed which corresponded to that observed for the oxidation of lucigenin's reduction product. The peak potential for the lucigenin reduction was found to be independent of pH in the pH range 4.7–10.0.

Coulometric studies on the lucigenin reduction wave gave a value of $n - 1$, over the potential range −0.3 to −1.0 V *vs.* Ag|AgCl. The coulometry was done at constant potential over this range at a platinum electrode in AN, DMF, and DMSO, where plating of the electrode by DBA is negligible. However, the final product of this reduction is DBA, a two-electron product. An esr signal, indicative of a radical, was observed when lucigenin was reduced in DMSO at a potential of −0.4 V. A scheme consistent with the above observations could be

$$\mathrm{Luc}^{2+} + e^- \rightleftarrows \mathrm{Luc}\cdot^+$$
$$\mathrm{Luc}^+ + \text{solvent} \rightarrow \mathrm{DBA} + \text{solvent}\cdot^+$$

However, it should be noted that more work is needed to definitively prove this to be the mechanism of the lucigenin reduction.

Production of Lucigenin ECL. All attempts to generate ECL under the conditions described by Tammamushi and Akiyama[11] failed. However, when a mercury pool was substituted for the platinum electrode and the

(14) A. Page and J. J. Lingane, *Anal. Chim. Acta*, **16**, 175 (1957).
(15) G. K. Turner, *Science*, **146**, 183 (1964).
(16) "TRW Fluorometry Handbook," TRW Instruments, El Segundo, Calif.

solution was unbuffered at pH 7, light could be observed. Oxygen was found to be necessary for the production of light, and furthermore no light was observed until the potential was sufficiently negative (−0.15 V) to reduce the oxygen. The oxygen reduction wave is at anodic potential relative to that of lucigenin in this system as can be seen from Figure 2, curve B. When a steady potential of −0.15 V was applied, the electrochemical reduction of lucigenin was not a significant process.

It is known that in basic solutions at a platinum electrode, oxygen is reduced *via* a multistep process, *occurring at the same potential*, to OH^-,[17] whereas in neutral solutions at mercury there are two, *well-separated* waves, the first of which is

$$O_2 + 2H_2O + 2e^- \rightarrow H_2O_2 + 2OH^-$$

Thus, when the reaction was run in basic solution at platinum, only OH^- was produced in the bulk of the solution, while under neutral conditions at mercury, hydrogen peroxide and OH^- were produced. The latter are the same reagents necessary for the "classical" production of lucigenin CL, and therefore the ECL observed under these conditions is simply the classical CL with two of the reactants supplied by the electrode reaction. In view of these facts, it is difficult to understand how Tammamushi and Akiyama were able to observe light under the conditions which they reported.

It was possible to produce lucigenin ECL in four nonaqueous solvents: EtOH, DMSO, DMF, and AN. Once again it was necessary to reduce oxygen, in this case to superoxide ($O_2 \cdot^-$),[18,19] before light was observed. It should be noted that due to size limitations in the cell holder used for the cell in Figure 1, a Pt reference electrode was used, and thus the potentials employed during the spectral studies do not correspond to those used when an Ag|AgCl reference was used.

In the case of nonaqueous solvents the potential necessary for oxygen reduction is more cathodic than for the lucigenin reduction as shown in Figure 2, curve A. Therefore, two processes are occurring at the electrode: Luc → DBA and $O_2 \rightarrow O_2 \cdot^-$. To ascertain which species were reacting, three experiments were run. First, a solution containing lucigenin in DMSO was bubbled with N_2 to exclude O_2, and the lucigenin was totally reduced to DBA. Then oxygen was bubbled through the solution. No light was observed. Second, a solution was used containing only DBA and oxygen. The oxygen was reduced to superoxide and once again no light was observed. Third, a solution containing only oxygen was used. The oxygen was electrolyzed to superoxide and a solution of lucigenin was admitted only after the electrolysis had been stopped. In this case light was observed. *These observations support the thesis that superoxide formed by the reduction of oxygen reacts only with lucigenin to cause light emission.*

Spectral Study of Lucigenin ECL. No ECL spectra were obtained for aqueous solutions due to rapid deposition of DBA on the cathode surface. The spectra obtained in nonaqueous solvents are shown in Figures 3–5. In all solvents except ethanol a two-component spectrum

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(18) D. L. Maricle and W. G. Hodgson, *Anal. Chem.*, **37**, 1562 (1965).
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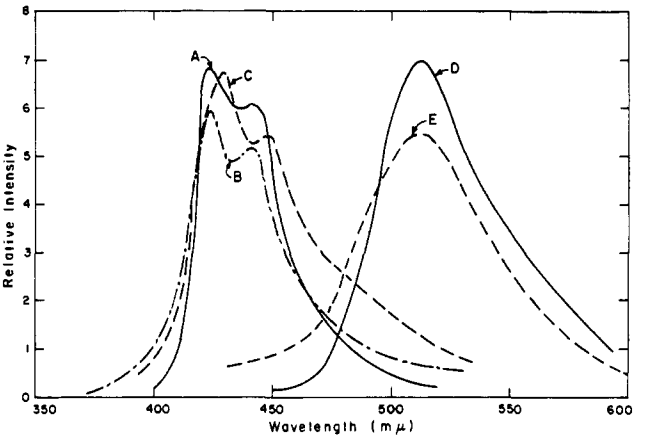

Figure 3. Spectra in DMSO and EtOH: (A) (—) fluorescence spectrum of 5×10^{-5} *M* NMA in DMSO; (B) (—·—) ECL spectrum in EtOH; (C) (- - -) ECL spectrum in DMSO at the beginning of electrolysis; (D) (——) fluorescence spectrum of 1×10^{-4} *M* DBA in DMSO; (E) (— — —) ECL spectrum in DMSO after 10 min of electrolysis.

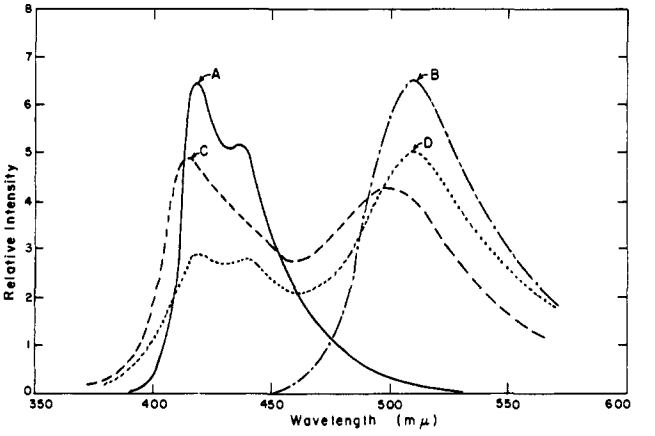

Figure 4. Spectra in DMF: (A) (—) fluorescence of 1×10^{-4} *M* NMA; (B) (—·—) fluorescence of 1×10^{-4} *M* DBA; (C) (— — —) ECL spectrum at beginning of electrolysis: (D) (···) ECL spectrum after 10 min of electrolysis.

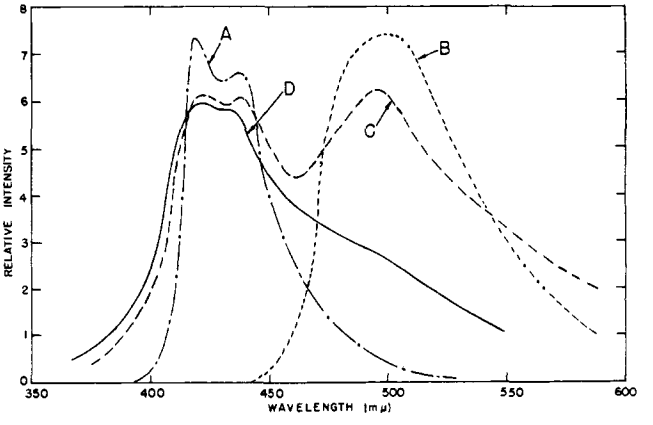

Figure 5. Spectra in acetonitrile: (A) (—·—) fluorescence of 5×10^{-5} *M* NMA; (B) (···) fluorescence spectrum of 1×10^{-5} *M* lucigenin; (C) (— — —) ECL spectrum at the beginning of electrolysis; (D) (——) ECL spectrum after 10 min of electrolysis.

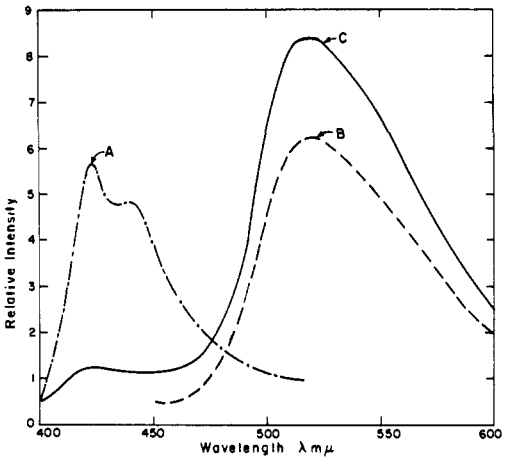

Figure 6. Fluorescence quenching and enhancement: (A) (—·—) fluorescence spectrum of 5×10^{-5} *M* NMA in DMSO excited at 375 mμ; (B) (— — —) fluorescence spectrum of 1×10^{-4} *M* DBA in DMSO excited at 375 mμ; (C) (——) fluorescence spectrum of 1×10^{-4} *M* DBA and 5×10^{-5} *M* NMA excited at 375 mμ.

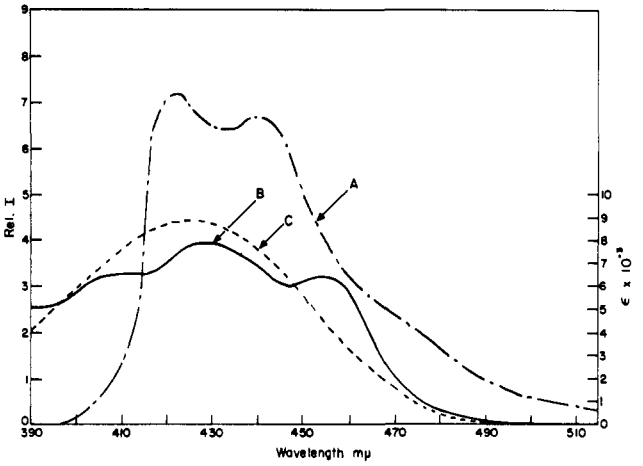

Figure 7. Fluorescence spectrum of NMA and absorption spectra of lucigenin and DBA showing overlap of donor fluorescence–acceptor absorption: (A) fluorescence of NMA (—·—); (B) absorption of lucigenin (——); (C) absorption of DBA (···).

was observed. The short-wavelength component corresponds to the emission from NMA, the primary emitter in the "classical" CL reaction.[5] A change in the intensity of the long-wavelength band with time of electrolysis was noted. The direction of change was different for the various solvents. Also, in DMF and DMSO the long-wavelength band corresponds to the fluorescence of DBA (λ_{max} 510 mμ) while in AN it corresponds to that of lucigenin (λ_{max} 500 mμ, broad peak).

Figure 3, curve B, shows the ECL spectrum in ethanol. The spectral distribution did not change as the time of electrolysis was increased, and the ECL spectrum corresponded entirely to the fluorescence of NMA. The ECL spectra obtained in DMF and DMSO are similar and appear in Figures 3 and 4 along with the fluorescence spectra of NMA and DBA in the respective solvents. At the beginning of the reaction the predominant emission is that of NMA as shown in Figure 3, curve C and Figure 4, curve C. After 10 min of electrolysis the emission is mainly that of DBA as seen in Figure 3, curve E and Figure 4, curve D. Figure 5 shows the various curves obtained in AN. In this solvent initially the emission is from lucigenin along with NMA, curve C, while after 10 min of electrolysis it is mostly that of NMA, curve D.

The observations reported above show that NMA is the molecule initially formed in the excited state by the CL process and thus is designated as being the primary emitter. Depending on the conditions of the reaction, either lucigenin or DBA acts as secondary emitters giving rise to the observed long-wavelength components in the ECL spectra. It thus appears that these secondary emitters are not formed in an excited state by a chemical reaction, but act as energy acceptors from the excited NMA formed in the ECL reaction.

Energy Transfer in the Lucigenin ECL. To investigate the extent of energy transfer in the ECL systems, fluorescence spectra were obtained for given concentrations of NMA and DBA in DMSO separately and together. These curves are shown in Figure 6. The results indicate energy transfer from excited NMA, but it is not possible by this method to distinguish between "trivial" re-absorption of NMA fluorescence or singlet–singlet energy transfer to the acceptor.

Fluorescence lifetimes for DBA and lucigenin in the various solvents were obtained. A shortened lifetime in a given solvent as compared to another indicates fluorescence quenching in that solvent. To further substantiate these lifetime measurements, the quantum efficiencies of fluorescence (Φ_F) in the various solvents were obtained. The lifetime and quantum efficiency data appear in Table I.

Table I. Fluorescent Lifetimes and Quantum Efficiencies[a]

Solvent	NMA τ (ns)	NMA Φ	DBA τ (ns)	DBA Φ	Lucigenin τ (ns)	Lucigenin Φ
H_2O	18.5	0.82	...	...	18.8	0.43
EtOH	14.1	0.61	4.0	0.45	<1	0.09
DMSO	9.0	0.49	4.9	0.58	<1	0.08
DMF	7.6	0.42	5.3	0.60	3.1	0.24
AN	7.2	0.35	3.2	0.40	24.7	0.72

[a] τ = fluorescence lifetime; Φ = fluorescence quantum efficiency.

If singlet–singlet energy transfer occurs in the NMA–DBA of NMA–lucigenin systems, then as the acceptor concentration is increased the observed lifetime of the donor should be shortened.[20,21] A plot of the reciprocal of the donor lifetime, $1/\tau$, *vs.* acceptor concentration should give a straight line with a slope equal to the rate constant for singlet–singlet energy transfer.[21] A series of such measurements were made and the plots of $1/\tau$ *vs.* acceptor concentration were found to be linear, and the rate constants derived from these plots appear in Table II.

Forster[22] has derived a theoretical relationship for dipole–dipole interaction resulting in energy transfer in which the "critical distance," R_0, for equal probability of transfer and deactivation by other processes is given by

(20) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965.
(21) W. R. Ware, *J. Am. Chem. Soc.*, **83**, 4374 (1961).
(22) Th. Forster, "Fluoreszenz Organisher Verbindungen," Vandenhoeck and Ruprecht, Gottingen, 1951.

Table II. Experimental and Theoretical Rate Constants for Energy Transfer and Critical Radius

Solvent	Lucigenin				DBA			
	k_{ET}[a]		R_0,[b] Å		k_{ET}[a]		R_0,[b] Å	
	Exptl	Theory	Exptl	Theory	Exptl	Theory	Exptl	Theory
DMSO	9×10^{10}	1.2×10^{11}	69	77	1.7×10^{11}	1.3×10^{11}	86	78
DMF	2×10^{11}	1.4×10^{11}	86	78	1.8×10^{11}	1.5×10^{11}	83	79
AN	1.4×10^{11}	1.6×10^{11}	74	77	1.5×10^{11}	1.7×10^{11}	76	78

[a] Rate constant for energy transfer. [b] Critical radius.

$$R_0^6 = \frac{9000(\ln 10)(2/3)^2\phi_D}{128\pi^5 n^4 N} J(\bar{\nu}) \quad (1)$$

where

$$J(\bar{\nu}) = \int f_D(\nu)\varepsilon_A(\nu)\frac{d\bar{\nu}}{\bar{\nu}^4} \quad (2)$$

and R_0 is related to the rate constant for energy transfer by

$$k_{ET} = \frac{R_0^3}{(7.35 \times 10^{-8})^3 \tau_D([A] = 0)} \quad (3)$$

where n is the refractive index of the solvent, N is Avogadro's number, ϕ_0 is the fluorescence efficiency of the donor in the absence of acceptor, f_D the donor fluorescence distribution in quanta normalized to unity on a wavenumber scale, $\varepsilon_A(\nu)$ is the molar decadic extinction coefficient of the acceptor, and ν is the wave number. The fluorescence spectrum of NMA and the absorption spectra of DBA and lucigenin in DMSO are shown in Figure 7 showing the favorable situation for energy transfer in these systems. Theoretical values of R_0 were calculated from these data along with those of Table I. The integral $J(\nu)$ was graphically evaluated. The theoretical values of R_0 calculated according to eq 1 also appear in Table II.

It should be noted that both the experimental and theoretical values for the rate constant of energy transfer (k_{ET}) are of the order of 10^{11} l./(mole sec), an order of magnitude faster than diffusion control, presenting good evidence for resonance singlet–singlet energy transfer in the systems NMA–DBA and NMA–lucigenin.

Figure 8 shows the results of calculations on the probability of energy transfer and trivial reabsorption from NMA to lucigenin in AN at various lucigenin concentrations. Curve C is the probability of energy being transferred *via* the resonance mechanism. Curve A is the resultant probability that excited NMA will behave normally, *i.e.*, either fluoresce or undergo internal conversion. Curve B is the probability of lucigenin absorbing a photon emitted by NMA. When curve A is multiplied by the quantum efficiency of NMA's fluorescence in AN and this product multiplied by curve B, curve D results, namely the probability of the trivial process occurring. Curve E is the sum of curves D and C or the total probability of energy being transferred, *via* either process. Note that at concentrations of *ca.* 5×10^{-4} *M* 50% of the excited NMA energy is transferred to lucigenin. Similar calculations were made for lucigenin and DBA in the various solvents studied. All showed 50% probability for total transfer at approximately the same concentration of acceptor as is shown in Figure 8. This is because extinction coefficients and k_{ET}'s of lucigenin and DBA are approximately the same. It should be noted from Figure 8 that at concentrations greater than 10^{-4} *M* the probability of energy transfer is greater than that for the trivial process.

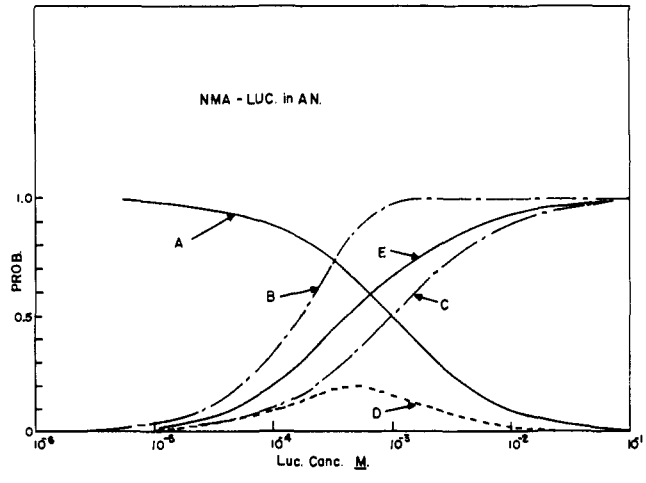

Figure 8. Probability curves for energy transfer and trivial reabsorption for NMA–lucigenin in acetonitrile: (A) (—) singlet excited NMA; (B) (— - —) lucigenin absorbing a photon of NMA fluorescence; (C) (—— -) energy transfer; (D) (- - - -) trivial reabsorption; (E) (——) sum of the trivial process and energy transfer.

Correlation of ECL Spectra with Quantum Efficiencies of Acceptor Fluorescence and Extent of Reaction. Since the data in Table II indicate that excited NMA transfers energy at about the same rate to either DBA or lucigenin in all of the solvents studied, the origin and intensity of the long-wavelength band in ECL is dependent only on the quantum efficiency of the acceptor fluorescence and the acceptor concentration. Thus, if the acceptor is present at a high concentration (10^4 *M*) and has a relatively high quantum efficiency, a long-wavelength band will be present. If, however, the acceptor concentration is low, no long-wavelength band will be observed. Also, when the quantum efficiency of the acceptor is low and its concentration is high, energy will be transferred to the acceptor, but because of radiationless deactivation only NMA emission will be observed. This idea correlates well with the ECL spectra shown in Figures 3–5 and the data of Table I.

In DMSO (Figure 3) the long-wavelength emission corresponds to DBA fluorescence. In this solvent lucigenin has a very low quantum efficiency of fluorescence (ϕ_f) of 0.08, whereas DBA has a ϕ_f of 0.58. Thus, when DBA is present at high enough concentrations, after it has been built up by electrochemical reduction of lucigenin, it is possible to observe secondary emission from DBA. Since the ϕ_f for lucigenin in DMSO is so small, no contribution due to emission from lucigenin is observed. The case of ECL in DMF shown in Figure 4 is similar to that in DMSO. In DMF lucigenin has a ϕ_f of 0.24 and DBA has a ϕ_f of 0.60. Some long-wavelength emission is observed at the beginning of the reaction in DMF, and

this is due to emission from lucigenin which in DMF fluoresces more efficiently than in DMSO.

In AN lucigenin has a high ϕ_f of 0.72 while DBA has a ϕ_f of 0.40. The long-wavelength emission in AN (Figure 5) is seen to be due to lucigenin emission, and this correlates well with the high ϕ_f of lucigenin in this solvent. In ethanol (Figure 3, curve B) lucigenin again has a very low ϕ_f of 0.09 and DBA has a ϕ_f of 0.45. However, DBA is fairly insoluble in EtOH. Thus the DBA concentration at all times is low, lucigenin is a poor emitter, and no long-wavelength emission is observed in EtOH.

The direction of change in the intensity of the long-wavelength band can also be explained. In the case of AN, lucigenin has a high quantum efficiency and is responsible for the long-wavelength emission. At the beginning of the reaction lucigenin is present at a relatively high concentration ($\sim 10^{-3}$ M) and the emission is intense. As the reaction proceeds the lucigenin concentration decreases and the intensity of the long-wavelength band likewise decreases. In DMSO and DMF, DBA is responsible for the emission at long wavelengths because lucigenin has a low quantum efficiency. At the beginning of the reaction there is little DBA present, and the long-wavelength emission is of low intensity, but as the reaction proceeds and DBA is built up, the emission at long wavelength increases.

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Thermal Decomposition of Tri- and Tetrasulfanes

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Abstract: An nmr technique has been employed to study the thermal decomposition of H_2S_3 and H_2S_4 in CCl_4 solution at 70.4° in the absence of oxygen. H_2S and elemental sulfur are found to be the ultimate reaction products. It is demonstrated, however, that sulfanes do not decompose directly into H_2S and elemental sulfur but rather form a variety of intermediate sulfanes. H_2S_4 is found to be more stable than H_2S_3. A free-radical mechanism for the reaction is proposed and a possible pathway for the formation of elemental sulfur is suggested.

The study of the thermal stabilities of a variety of polysulfidic chain containing compounds has led to a better understanding of the nature of the sulfur–sulfur bond and of the factors governing the physical and chemical properties of molecules containing sulfur–sulfur linkages. Nevertheless, the understanding of the sulfur–sulfur bond is far from complete. The bond dissociation energies presented in Table I establish that the energy required to break a given sulfur–sulfur bond depends largely on the position of the bond in the sulfur chain of a given system. Thus the central sulfur–sulfur bond in MeS_4Me requires less energy to break than the oxygen–oxygen bond in the relatively unstable hydrogen peroxide. Furthermore, the nature of the group terminating the polysulfide chain seems to have at least some effect on the strength of a given sulfur–sulfur bond in species of the same sulfur chain length.

Thermal stabilities of alkyl polysulfides of varying sulfur chain length have been investigated by several authors (see citations in ref 1), but it was not until the advent of the nmr analytical method that reliable quantitative data on the decomposition products could be obtained.

Thus Tobolsky, *et al.*[1] studied the thermal decomposition of methyl polysulfides by the nmr analytical method. In the early stages of the thermal decomposition of MeS_4Me the main product found was MeS_3Me, while MeS_5Me was found in smaller quantities. These authors postulated a free-radical mechanism initiated by the thermal disproportionation of the parent polysulfide into two resonance-stabilized radicals according to the equation

$$MeS_4Me \overset{80°}{\rightleftharpoons} 2MeS_2\cdot \quad (1)$$

The propagation reactions involved the subsequent attack of these initial radicals on the sulfur chain of the parent polysulfide according to the reaction

$$MeS_4Me + MeS_2\cdot \rightarrow MeS_3Me + MeS_3\cdot \quad (2)$$

followed by termination reactions of the type

$$MeS_2\cdot + MeS_3\cdot \rightleftharpoons MeS_5Me \quad (3)$$

This reaction scheme was postulated to account for the fact that no MeS_2Me had been formed, which would have indicated that $MeS\cdot$ radicals were involved. It was, therefore, concluded that the initial homolytic reaction 1 was more likely than the reaction

$$MeS_4Me \rightleftharpoons MeS\cdot + MeS_3\cdot \quad (4)$$

presumably because the central bond in MeS_4Me is weaker than the other two sulfur–sulfur bonds in this molecule (Table I).

MeS_3Me was found to be considerably more stable than MeS_4Me.[1] This was rationalized by noting that

(1) T. L. Pickering, K. J. Saunders, and A. V. Tobolsky in "The Chemistry of Sulfides," A. V. Tobolsky, Ed., Interscience Publishers, New York, N. Y., 1968.