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Chemiluminescent Electron-Transfer Reactions of Radical Anions

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Abstract: Studies of the chemiluminescent reactions of the 9,10-diphenylanthracene radical anion with 9,10-dichloro-9,10-dihydro-9,10-diphenylanthracene and benzoyl peroxide are reported. The luminescence corresponds to the fluorescence of the parent anthracene. Other radical anions undergo similar luminescent reactions with benzoyl peroxide and toluenesulfonyl chloride. Oxidation of the radical anion of N-phenylcarbazole apparently leads to phosphorescent emission from the triarylamine. The formation of electronically excited molecules is explained by reactions involving only the transfer of an electron from the radical anion to another radical which serves as an oxidizing agent in a process related to recombination luminescence.

The reactions of radical anions derived from fluorescent compounds with various oxidizing agents appear to represent a very general type of chemiluminescent reaction.[1] We believe that most of these reactions can be rationalized on the basis of the experimental results available at present although no kinetic data or photon yields are available.

Luminescent reactions in solution which are bright enough to be seen easily are uncommon. It seems that most reactions which liberate sufficient energy to produce a product molecule in an excited state do so rarely if at all. This may be the case because the energy is liberated relatively slowly as the transition state is traversed and becomes distributed among many bond vibrations which makes it unavailable for electronic excitation. It is conceivable that a concerted reaction in a small molecule or in a small section of a large molecule might not be subject to these restrictions and could be luminescent. If the energy liberated by a chemical transformation were to appear in a time that is short on a molecular vibration time scale, the conservation of energy might require one of the products to be formed in an accessible excited electronic state because the energy cannot be dissipated quickly enough as thermal energy. Electron-transfer reactions are good candidates for the latter situation. Because little or no bond reorganization is required, one might expect such a reaction to be a diffusion-controlled process which occurs as soon as the electron clouds of the reactants overlap appreciably. The annihilation of aromatic hydrocarbon radical cations and radical anions is a fairly well understood example of such an electron-transfer reaction. Recent studies have provided support for the view that the transfer occurs on direct collision of the reactants and, in suitable cases, leads to the formation of an excited dimer.[2] It is necessary that the energy of the reaction be sufficient to account for the observed chemiluminescence, and this has been shown to be true for some of the hydrocarbon ion reactions. The energies of the luminescent steps of the reactions discussed in this paper cannot be determined directly, but reasonable estimates can often be made and shown to be consonant with the mechanisms proposed. In all of our discussions we shall neglect the effects of solvation and ion-pair formation. The only justification, albeit an unsatisfactory one, that can be offered is that we are dealing with fairly large molecules with diffuse charge

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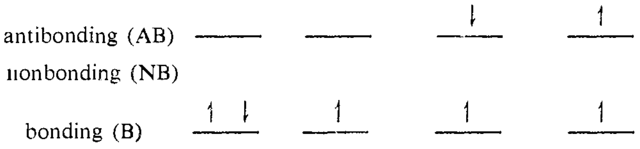
[1] E. A. Chandross and F. I. Sonntag, *J. Am. Chem. Soc.*, **86**, 3179 (1964).

[2] E. A. Chandross, J. W. Longworth, and R. E. Visco, *ibid.*, **87**, 3259 (1965).

distributions which would decrease the importance of such effects.

Recombination luminescence is a known phenomenon which is basic to the understanding of much that we will be discussing. It was originally discovered in Lewis' laboratory[3,4] and has been studied in several other laboratories. Exceptionally long-lived, generally phosphorescent, afterglows are observed when rigid solutions (77°K) of any of several easily ionizable species are irradiated by ultraviolet light. Lewis and Bigeleisen suspected a photoionization process and were able to identify the radical cation of triphenylamine when the latter was subjected to these conditions. It now appears that photoionization may be a fairly common event which often proceeds *via* a two-photon process involving ionization of the triplet state.[5–7] We are more concerned, however, with the reversal of the process which occurs when the previously ejected electron acquires enough thermal energy to allow its removal from a trap in the glassy solvent and its return to the parent molecule. A large amount of energy is liberated as the electron returns and, perhaps, because it cannot be converted to vibrational energy fast enough, causes the electron to return to an excited level rather than to the ground state. It is as yet unknown why delayed phosphorescence is generally observed and delayed fluorescence is rarely seen.[8] Linschitz and co-workers have suggested[9] that this may be a consequence of the relative geometries of the various states. A simple MO diagram may be drawn to illustrate the process.



$$R \xrightarrow{2h\nu} e^- + R^+ \longrightarrow {}^1R^* \text{ and/or } {}^3R^*$$

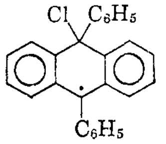
The chemiluminescent reaction of Ar^+ and Ar^- appears to be directly related to recombination luminescence with Ar^- serving as a source of electrons of appropriate energy. Only a few hydrocarbons have been studied in detail, but many fluorescent hydrocarbons exhibit chemiluminescence upon low-voltage alternating current electrolysis under appropriate conditions, and the reaction seems to be a general one.[2,10]

We have studied the reactions of the radical anions derived from various aromatic hydrocarbons and other fluorescent species with a variety of oxidizing agents and found that chemiluminescence in these systems is a much more common phenomenon than might have been expected. Radical anions tend to react as electron donors rather than as nucleophilic reagents, and their chemistry can usually be rationalized in terms of initial electron transfer followed by subsequent reactions of radicals produced upon reduction of the other reactant.[11] The reactions of 9,10-diphenylanthracene (DPA) derivatives have been studied fairly extensively. The DPA skeleton was chosen for several reasons. It has a good fluorescence efficiency in solution (~80%),[12] and it is a stable species whose most reactive centers (9 and 10) in DPA, DPA^+, and DPA^- are sterically hindered by phenyl groups which also allow additional charge and spin delocalization. These factors should favor simple electron transfer rather than bond formation. We were unable to study the reaction of DPA^+ and DPA^- in a chemical system because DPA^+ is quite unstable, having a lifetime of only about a minute even when generated by electrooxidation in pure acetonitrile.[13] On the other hand, DPA^- can be prepared easily by reacting excess hydrocarbon with metallic sodium, potassium, or lithium in tetrahydrofuran or 1,2-dimethoxyethane solution.[14]

The Chemiluminescent Reaction of DPA^- with DPA Dichloride. The reaction of DPA^- (K^+ or Na^+ salt) with 9,10-dichloro-9,10-dihydro-9,10-diphenylanthracene ($DPACl_2$), a species whose formal oxidation state is that of DPA^{+2}, is chemiluminescent and yields DPA. The spectrum of the emitted light is identical with the normal fluorescence spectrum of DPA. We consider the following mechanism to be the most reasonable one consistent with the available data.

$$DPA^- + DPACl_2 \longrightarrow$$

$$DPA + Cl^- + DPACl\cdot =$$



$$DPACl\cdot + DPA^- \longrightarrow DPA + DPA^* + Cl^-$$

When the reaction is carried out with a few grams of material in glyme (0.5 l.), a transient, deep yellow-orange color, attributable to DPACl·, appears and then fades as the approximately stoichiometric (2:1) amount of DPA^- is added. The total reaction product, after removal of a water-soluble precipitate (KCl), appeared to be DPA contaminated by $DPACl_2$. When treated with HI in hot acetic acid it gave pure DPA.

The second step in the above sequence might proceed through a transition state resembling $DPACl^-$. To simplify the problem let us consider only the central ring of the anthracene system, ignoring the outer rings and the phenyl groups at the 9 and 10 positions. The injection of an electron by DPA^- into DPACl· can yield $DPACl^{-*}$ if the electron enters the lowest antibonding level of the pesudopentadienyl radical DPACl·. The additional energy liberated by the subsequent or perhaps concomitant departure of a chloride ion, which must be accompanied by the transformation of the pentadienyl system into a benzenoid system, may result in the direct formation of an excited state of the product molecule. Thus

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(3) G. N. Lewis and J. Bigeleisen, *J. Am. Chem. Soc.*, **65**, 2424 (1943).

(4) See also G. N. Lewis and M. Kasha, *ibid.*, **66**, 2100 (1944), and references therein.

(5) W. A. Gibbons, G. Porter, and M. I. Savadatti, *Nature*, **206**, 1355 (1965).

(6) K. D. Cadogan and A. C. Albrecht, *J. Chem. Phys.*, **43**, 2550 (1965), and references therein.

(7) B. Stevens and M. S. Walker, *Chem. Commun.* (London), 8 (1965).

(8) B. Brocklehurst, G. Porter, and J. M. Yates, *J. Phys. Chem.*, **68**, 203 (1964).

(9) H. Linschitz, M. G. Berry, and D. Schweitzer, *J. Am. Chem. Soc.*, **76**, 5833 (1954).

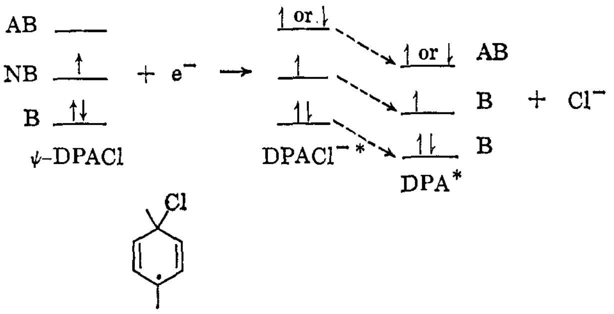
(10) D. M. Hercules, *Science*, **145**, 808 (1964).

(11) D. J. Morantz and E. Warhurst, *Trans. Faraday Soc.*, **51**, 1378 (1955); G. E. Coates, "Organometallic Compounds," John Wiley and Sons, Inc., London, 1960, p 32 ff; B. J. McClelland, *Chem. Rev.*, **64**, 301 (1964).

(12) W. H. Melhuish, *J. Phys. Chem.*, **65**, 229 (1961).

(13) R. E. Visco and E. A. Chandross, unpublished work.

(14) *Cf.* R. Gerdil and E. A. C. Lucken, *Helv. Chim. Acta*, **44**, 1966 (1961).



Alternatively, it has been suggested[15] that DPACl· might ionize to DPA$^+$ and Cl$^-$ and that the reaction might be a simple Ar$^+$–Ar$^-$ reaction. However, the solvents used have fairly low (<10) dielectric constants, and the DPA$^+$ and Cl$^-$ ions would be associated with each other; we are then arguing about the length of a C–Cl bond and its ionic character. We do not believe that there is much to be gained at this time by advancing detailed speculations, and we would prefer to consider the over-all effect of the process which is the injection of an electron into DPACl· followed by the departure of Cl$^-$ and the formation of DPA*. This process is related to recombination luminescence but is more complex because an ion must be lost before the excited product molecule can be formed. There is no way of predicting the ratio of triplet excitation to singlet excitation or of either to vibrationally excited ground-state molecules. This will depend on the relationships among the various energy surfaces and possible differences in activation energies. If the relation were a simple statistical one, we would expect 75% of the excited product molecules to be triplets,[5,8] and these would probably not yield radiation unless high local concentrations were available to permit triplet–triplet annihilation.[16] We had felt that triplet–triplet annihilation was not likely to be an important process because of the presence of quenchers in these systems. Some of our results have forced us to reconsider our views regarding the intermediacy of triplets, and we shall discuss this point further toward the end of the paper. We have no experimental results bearing on the question of triplets in most of our work, and we shall talk in terms of the direct formation of excited singlet states unless the data require the presence of triplets. The formation of a reaction product as a triplet is different from that as the excited singlet mainly because of multiplicity, and one may consider the formation of excited electronic states rather than of vibrationally excited ground states to be of paramount interest.

A reaction which may be analogous to the reaction of DPA$^-$ and DPACl$_2$ is that of sodium naphthalenide with this dichloride which also yields light identified visually as DPA fluorescence. The same explanation can be advanced here, substituting $C_{10}H_8^-$ for DPA$^-$, but one cannot overlook a trivial explanation; the reaction $C_{10}H_8^- + \text{DPA} \rightarrow C_{10}H_8 + \text{DPA}^-$ is an exothermic one. One cannot distinguish between the two possibilities.

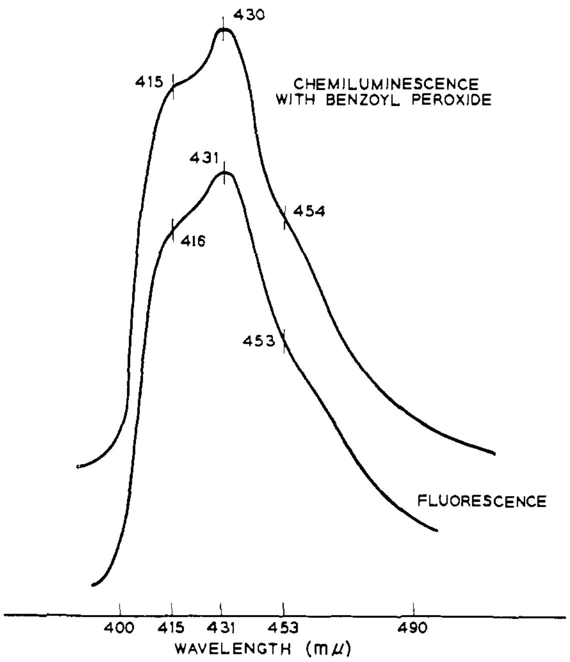


Figure 1. Chemiluminescence and fluorescence spectra of 9,10-diphenylanthracene.

The Chemiluminescent Reaction of DPA$^-$ with Benzoyl Peroxide. It turns out that the reactions of several other reagents with DPA$^-$ are chemiluminescent. These include benzoyl peroxide, *p*-toluenesulfonyl chloride, *p*-toluenesulfonic acid anhydride, methanesulfonyl chloride, oxalyl chloride, and chlorine. Our most detailed studies are of the benzoyl peroxide reaction. The sole nonacidic product of this reaction is DPA which is virtually as pure as the hydrocarbon used for the preparation of DPA$^-$. The chemiluminescence spectrum corresponds to the normal fluorescence spectrum of DPA (Figure 1).

The luminescence produced by this reaction is easily visible upon the addition of a tiny drop of 0.01 *M* DPA$^-$ solution, which contains about 10^{-7} mole of DPA$^-$, to a dilute solution of benzoyl peroxide. It is noteworthy that DPA$^-$ yields chemiluminescence upon addition to an ethanol solution of benzoyl peroxide. No luminescence is observed in the absence of the peroxide. Radical ions are destroyed extremely rapidly by hydroxylic solvents, and this observation indicates that the activation energies for the luminescent reaction sequence must be very low.

We have previously mentioned the tendency of radical anions to act as electron donors. The first step in the reaction of DPA$^-$ with benzoyl peroxide (BPO) is likely to involve the transfer of an electron from DPA$^-$ to the more electrophilic BPO (mechanism I). The electrolytic reduction of BPO in acetonitrile is irreversible, and a potential for the BPO/BPO$^-$ couple cannot be assigned. However, a large current is drawn at an electrode (Pt) potential of -1 v *vs.* sce, and one may infer from this that the electrode potential is less negative than -1 v.[17] The reduction of DPA occurs at -1.9 v and thus step 1 cannot yield more than 0.9 ev (21 kcal), far too little to account for DPA fluorescence which has peaks at 435 mμ (2.9 ev) and 410 mμ (3.1 ev). It is also possible that a radical ion such as BPO$^-$ would be a fluorescence quencher.

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(15) We are indebted to Professor D. M. Hercules of the Massachusetts Institute of Technology for suggesting this mechanism to us.

(16) C. A. Parker and C. G. Hatchard, *Proc. Chem. Soc.*, 147 (1962); *Proc. Roy. Soc.* (London), **A269**, 470 (1962).

(17) We are indebted to Dr. R. E. Visco for performing these experiments and for educational discussions of their significance.

Mechanism I

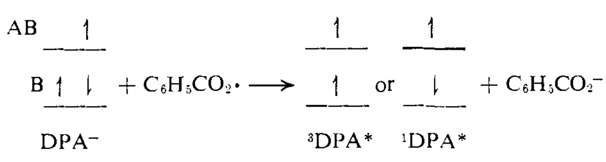
$$DPA^- + BPO \longrightarrow DPA + BPO^- \quad (1)$$

$$BPO^- \longrightarrow C_6H_5CO_2^- + C_6H_5CO_2\cdot \quad (2)$$

$$DPA^- + C_6H_5CO_2\cdot \longrightarrow DPA^* + C_6H_5CO_2^- \quad (3)$$

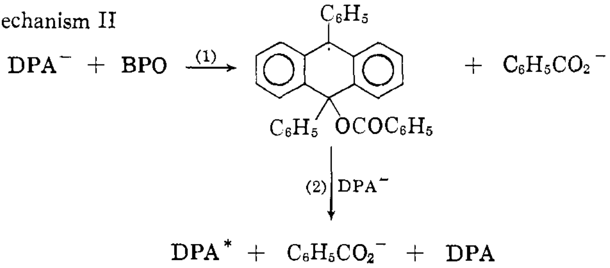
We suggest that BPO^- is unstable, as indicated by the electrochemical data, and fragments readily into a benzoate ion and a benzoate radical (step 2). This is followed by the transfer of an electron from another molecule of DPA^- to the benzoate radical and yields DPA*. Unfortunately the potential for the benzoate ion–benzoate radical couple in aprotic media is not known. We tried to learn something about this transformation by studying the oxidation of benzoate ion. Tetramethylammonium benzoate in acetonitrile solution does not exhibit any oxidation current on a platinum electrode up to a potential of +2 v *vs.* sce where either solvent or electrolyte (tetrabutylammonium perchlorate) breakdown begins. Even though the benzoate ion–benzoate radical couple may be irreversible under these conditions, one may infer from this negative evidence that the oxidation potential of benzoate ion is at least +1.5 v.[17] This yields a minimum of 3.4 ev for step 3 which is sufficient for it to be energetically feasible.

Step 3 can be discussed further in various ways. It may, as in recombination luminescence, involve the capture of a sufficiently energetic electron by a benzoate radical which yields an excited benzoate ion. This would be followed by the transfer of the energy to the nearby DPA. The formation of an excited benzoate ion would require about 3.8 ev, which may be more than is available from step 3. Even if step 3 cannot provide enough energy to form $^1(C_6H_5CO_2^-)^*$, it may go as written if the formation of an excited electronic state is favored by the rapidity with which the energy is released, as discussed earlier. In any case it seems probable that the conversion of an activated complex into products, one of which is in an excited electronic state, would result in the excitation being localized in the molecule having the lowest lying level before the complex breaks up. The situation is complicated by the unknown relationships among the various energy surfaces of possible intermediates and by the possibility that the intrusion of solvent or the counterion might influence the liberation of the energy as vibrational energy (eventually thermal) rather than as electronic energy. The above process (mechanism I), coupled with the assumptions that the formation of triplets *vs.* singlets is statistical and that triplet–triplet annihilation does not occur, puts the upper limit of the photon yield at 12.5%, based on DPA^-. The *net* effect of either path is the removal of an electron from the highest bonding level of DPA^- rather than the electron in the antibonding level. Thus



There is another reasonable mechanism which may be advanced to explain the chemiluminescent reaction of DPA^- with BPO. It is analogous to the mechanism which was suggested for the DPA^-–$DPACl_2$ reaction

Mechanism II



The first step is a nucleophilic attack by the radical anion on a peroxidic oxygen atom of BPO which generates a radical related to the DPACl· radical previously postulated. This radical could then react with another DPA^- as indicated. However, some experimental results contradict this hypothesis. DPA^- reacts instantly with lauroyl peroxide, an aliphatic analog of BPO, but no light is discernible. If mechanism II or a simple variant of it were operative, we would not expect such a large difference in behavior. Mechanism I, on the other hand, provides a reasonable explanation for this discrepancy. The lifetime of an arylcarboxylate radical is much longer than that of an alkylcarboxylate radical,[18] and if lauroyloxy radicals were formed most of them might decarboxylate before they could react with DPA^-. It is reasonable to assume that the various alkyl radicals resulting from the decarboxylation of the lauroyloxy radical would not yield luminescent reactions. Another observation which weakens mechanism II is the failure of both 9,10-diacetoxy-9,10-dihydro-9,10-diphenylanthracene and the corresponding dibenzoyloxy compound to undergo a luminescent reaction with DPA^-. These compounds would be expected to produce either $DPAOCOCH_3\cdot$ or $DPAOCOC_6H_5\cdot$ radicals as intermediates. The unknown but presumably *trans* configuration of these esters is unlikely to be an important factor. We have not been able to obtain the dibenzoate as analytically pure material, but the failure of this compound to give any light upon reaction with DPA^- is significant. These observations make mechanism II a rather untenable hypothesis. There is no obvious reason why these reactions are not luminescent, assuming that sufficient energy is available.

Other Chemiluminescent Reactions of DPA^-. Several other chemiluminescent reactions of DPA^- which appear to produce DPA* may be rationalized by mechanisms similar to those proposed for the DPA^-–$DPACl_2$ and DPA^-–BPO reactions. Thus, the reaction with chlorine probably involves the DPACl· radical discussed previously. Similarly oxalyl chloride and mercuric chloride might serve as chlorinating agents.

$$DPA^- + ClCOCOCl \longrightarrow DPACl\cdot + 2CO + Cl^-$$

$$DPA^- + HgCl_2 \longrightarrow DPACl\cdot + (HgCl)^- \longrightarrow Hg + Cl^-$$

The toluenesulfonyl chloride reaction might also be explained on this basis since this acid chloride is known to act occasionally as a chlorinating agent and could react with DPA^- to form DPACl·. Alternatively, one can visualize a process similar to that proposed for the BPO reaction (mechanism I).

$$DPA^- + C_7H_7SO_2Cl \longrightarrow DPA + C_7H_7SO_2\cdot + Cl^- \quad (1')$$

$$C_7H_7SO_2\cdot + DPA^- \longrightarrow DPA^* + C_7H_7SO_2^- \quad (2')$$

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(18) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, Chapter 10.

This explanation has the virtue of being readily extensible to the luminescent reaction of DPA^- with toluenesulfonic acid anhydride, which we feel is not likely to proceed *via* a nucleophilic displacement.

Chemiluminescent Reactions of N-Methylacridone Ketyl. The hypotheses advanced to explain the luminescent reactions of DPA^- can be extended directly to the chemiluminescent reactions of the sodium ketyl of N-methylacridone. Ketyls are known to be oxidized easily to their ketone precursors and appear even less likely than aromatic hydrocarbon anions to react as nucleophilic reagents. There are relatively few fluorescent ketones. N-Methylacridone was chosen because it is a particularly stable compound and is easily prepared, factors which compensate for the disadvantage of having a poor fluorescence yield. The ketyl undergoes chemiluminescent reactions with toluenesulfonyl chloride and benzoyl peroxide in glyme. The emission spectrum of the latter reaction is virtually identical with the normal fluorescence spectrum (λ_{max} 420 mμ) of the acridone. The product of this reaction is pure acridone, and we were not able to find any phenolic materials which would have arisen through nuclear attack by the oxidant.

Chemiluminescent Reactions of the N-Phenylcarbazole Radical Anion. Another type of compound that was potentially different in behavior was the radical anion derived from a species which is easily oxidized itself. Such a radical anion could act as a very powerful reducing agent. A triarylamine seemed appropriate and we selected N-phenylcarbazole. It would be expected to behave like triphenylamine and, as it is a fairly rigid molecule, it ought to have a higher fluorescence efficiency than the latter.[19] N-Phenylcarbazole reacts readily with sodium in glyme, giving a deep blue solution. This solution, which undoubtedly contains the desired radical anion, gives a bright blue chemiluminescence with all of the "usual" oxidizing agents. The formation of electronically excited molecules can be explained by mechanism I, advanced for the reactions of DPA^-, but the luminescence is unusual because the fluorescence of N-phenylcarbazole lies almost entirely in the ultraviolet (λ_{max} 365 mμ) and is nearly invisible to the eye. The chemiluminescence spectrum (Figure 2) of the benzoyl peroxide reaction revealed that two emission bands were present. One of the bands (λ_{max} 365 mμ, shoulder at 356) strongly resembles the fluorescence of N-phenylcarbazole; the second, more intense band occurs at λ_{max} 410 and 430 mμ and is responsible for the visual brightness of the reaction. The reaction of the anion with toluenesulfonyl chloride gave only the long-wavelength band. The nonacidic product of this reaction was fairly pure N-phenylcarbazole; its infrared spectrum differed but little from the starting material. The crude product did not show any appreciable fluorescence at 430 mμ nor did the solution immediately after the reaction was over. There is a very weak fluorescence at 430 mμ in the N-phenylcarbazole we used, but it is so weak that it is not a likely source of the chemiluminescence. We do not yet know with certainty what reaction or species is responsible for the 430-mμ band, but there are two hypotheses which can be considered. The similarity of the shape of the band to that of the phosphorescence spectrum of N-phenylcarbazole is striking, although the latter (Figure 2, measured for a glassy solution at 77°K) is shifted to longer wavelength by about 10 mμ and has a band at 465 mμ which would have to correspond to a shoulder in the chemiluminescence spectrum. It would be quite unusual if a phosphorescent emission were the source of luminescence in solution at 25°, and we have been rather reluctant to advocate this explanation. However, evidence presented during the last few years by different research groups has indicated that one can observe triplet–singlet emission if one looks very carefully for it or if one simply has a sufficiently high concentration of triplets, two variations of the same principle. Parker and Hatchard[20] have observed the phosphorescence of solutions of phenanthrene. A more striking series of results is that of Vasil'ev, *et al.*,[21] who have observed ketone phosphorescence during the oxidation of hydrocarbons by oxygen, which is also an extremely effective quencher of triplets. It now appears that phosphorescence will have to be considered seriously as a source of chemiluminescence, particularly in dim systems. We are suggesting it as a source of a fairly bright emission which would require the formation of a large number of triplets so that a reasonable fraction could survive long enough to radiate. We are still not completely happy about this explanation, but we feel that it is a reasonable one. It is conceivable that the triplets may not be normal triplets but may have a shortened lifetime because of catalysis of radiative intersystem cross-

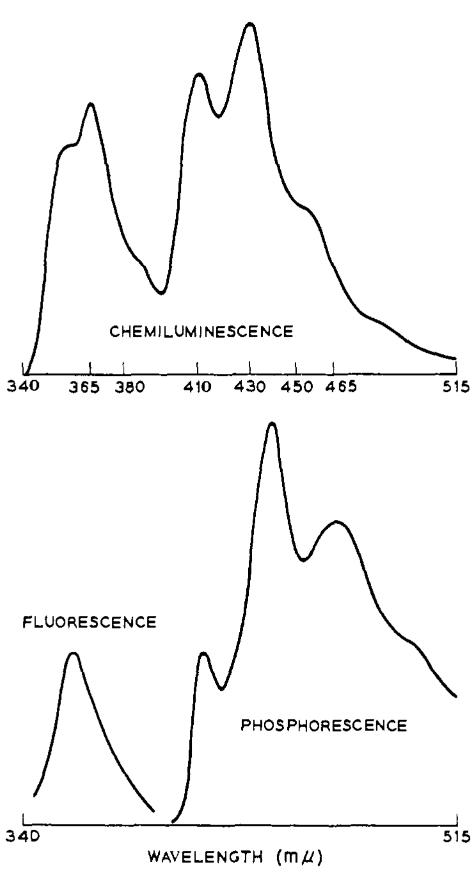

Figure 2. Spectra of N-phenylcarbazole.

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[19] W. West in "Chemical Applications of Spectroscopy," W. West, Ed., Interscience Publishers, Inc., New York, N. Y., 1956.

[20] C. A. Parker, *Advan. Photochem.* **2**, 305 (1964).

[21] R. F. Vasil'ev, *et al.*, *Opt. Spectry.* (USSR), **18**, 234 (1965).

ing by another material present in the solution. This could increase the phosphorescence yield in fluid solution. We intend to investigate this point further.

The assignment of one of the bands in the chemiluminescence spectrum of the N-phenylcarbazole anion to a phosphorescent transition requires that triplet–triplet annihilation be reconsidered as a source of fluorescent radiation in these systems. The formation of triplets *via* electron-transfer reactions of the type that we have discussed is very similar to the formation of excited singlets; two doublet states can yield either a singlet or a triplet. The latter requires less energy and this may be an important factor. However, there is still no evidence bearing on the question of triplets in most of these reactions, and we do not feel that any further discussion of this point is justified at this time.

A second explanation for the N-phenylcarbazole results is based on the ease of oxidation of triarylamines. One may postulate the following series of reactions whose conclusion is the formation of an excimer of N-phenylcarbazole which could be responsible for the long-wavelength emission.

$$\left.\begin{aligned} &\mathrm{N{-}PhC^- + C_7H_7SO_2Cl \longrightarrow N{-}PhC + C_7H_7SO_2\cdot + Cl^-} \\ &\mathrm{N{-}PhC + C_7H_7SO_2\cdot \longrightarrow N{-}PhC^+ + C_7H_7SO_2^-} \end{aligned}\right\} \text{one step?}$$

$$\mathrm{N{-}PhC^+ + N{-}PhC^- \longrightarrow (N{-}PhC)_2^*}$$

The existence of an excimer shoud be verifiable by studying the fluorescence spectrum of N-phenylcarbazole as a function of concentration. We examined the fluorescence over the range of 10^{-3} to 1 M and found that the spectral distribution does not change appreciably as the concentration increases although self-quenching is evident. However, this negative evidence for the formation of an excimer upon irradiation is not necessarily applicable to the situation prevailing in the chemiluminescent reaction medium. It may well be that the formation of an excimer requires activation energy which is available from the reaction of Ar^+ and Ar^- but is not available during the encounter of Ar^* with Ar. We have recently shown[2] that the reaction of Ar^+ and Ar^- does favor excimer emission, and the observed long-wavelength emission is in a reasonable place for excimer radiation. Unfortunately, the band shape is not like that of any known excimer. These loosely bound molecular complexes always exhibit broad structureless fluorescence bands which do not resemble our structured band. Also, the bulky out of plane phenyl substituent should make excimer formation a difficult process. We do not consider this hypothesis to be a likely one in view of these objections.

We made several attempts to prepare the cation radical of N-phenylcarbazole and obtained low yields of dark solid reaction products.[22] The epr spectra of two of these samples were not encouraging; they consisted of only a single line with no evidence of nitrogen splitting. These solids gave a weak chemiluminescence with the radical anion, but we do not regard this observation as significant.

We have also made qualitative studies of a few other hydrocarbons and heterocyclic compounds. We have had no difficulty in observing luminescence from anions derived from hydrocarbons which fluoresce in the visible. We were not able to detect any chemiluminescence from the reaction of the sodium derivatives of either 1,3,5-triphenylbenzene or naphthalene. The reason may be a combination of decreased fluorescence yield[19] and/or instrument sensitivity or simply that the reaction does not provide enough energy to allow the formation of these species in an excited singlet state. The fluorescence maximum of 1,3,5-triphenylbenzene is at 350 mμ (3.6 ev), but the fluorescence yield is probably low because of the nonrigid geometry of this species; naphthalene fluorescence requires a somewhat higher energy (*ca.* 4 ev). It appears that the results obtained with chemically prepared anions are closely related to those obtained in electrochemical systems but are more complex. We believe that the oxidations of radical anions derived from fluorescent systems represent a very general class of chemiluminescent reaction which is similar in its basic nature to the known phenomenon of recombination luminescence. The major problem is the selection of the oxidizing agent. Ideally, we require a sufficiently energetic one-electron acceptor such that neither it nor its reduction product is a fluorescence quencher. This set of requirements is probably self-contradictory more often than not, and thus it appears that one will have to be content with low concentrations of oxidant generated *in situ*.

In conclusion, we recognize that the explanations proposed to interpret our observations are not rigorously established. We do believe that they form a self-consistent set and that they are the most reasonable explanations available. We cannot propose any alternative simple mechanisms which can account for the data. A more detailed explanation awaits the availability of kinetic data and photon yields and, in the case of N-phenylcarbazole, positive identification of the emitting species. We feel that kinetic data will be difficult to obtain because of the likelihood of unstable intermediary compounds and the necessity of using solvents which may not be sufficiently inert to the reaction conditions.

Experimental Section[23]

The Flow-System Chemiluminescence Spectrometer. We originally began the construction of this apparatus because we wanted an instrument which used a flow system so that we could study the emission spectrum of a reaction before any appreciable concentration of products built up and perhaps interfered with the reaction or influenced the light emission. The reactions discussed in this paper are extremely rapid and a flow system device is a necessity. A schematic diagram of the apparatus is presented in Figure 3. The radical-anion solution was loaded into a syringe which employed a Teflon-tipped plunger requiring considerably more force for movement than a conventional syringe. The plunger was driven upward by a screw which in turn was driven by a synchronous motor. The solution was injected into the cell through a 28-gauge needle at a rate of about 2 ml/min and generally gave a "flame" directly on top of the end of the needle. The solution of the oxidizing agent was flowed through the cell which was essentially a 1-mm ultraviolet absorption cell. At first we made arrangements to maintain a constant gravity head in the oxidant reservoir, but this turned out to be unnecessary because we could scan the emission spectrum in less than a minute and the flow was essentially constant during this time. A determination of light intensity *vs.* time gave a variation of no more than ±2–3% (gradual) over a minute or so and this is sufficiently accurate for our needs. We used a Bausch and Lomb grating monochromator

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[22] *Cf.* E. Weitz and H. W. Schwechten, *Ber.*, **59**, 2307 (1926).

[23] All reactions were run under a nitrogen atmosphere; melting points are corrected.

and a Photovolt photometer with a 1P21 photomultiplier. It is possible to obtain fluorescence spectra with this apparatus and a simple ultraviolet lamp, but occasionally we used an Aminco-Keirs spectrometer equipped with a 1P28 photomultiplier. The spectra have not been corrected for photomultiplier response.

Purification of Solvents. Dioxane, 1,2-dimethoxyethane (DME), or tetrahydrofuran (THF) was boiled with excess sodium metal under nitrogen for an indefinite period of time, usually 16–24 hr. Then benzophenone was added and the mixture was refluxed until the deep blue color of the ketyl had become violet, indicating at least partial reduction to the dianion of benzophenone. After refluxing for an additional hour or two, the solvent was distilled and stored in tightly closed dark bottles. The ethers remained quite pure for at least 2 months as judged by the rapidity with which sodium reacted with aromatic hydrocarbons in such a solvent. Transfers were made with hypodermic syringes under a nitrogen atmosphere. This has proved to be a very convenient way to transfer materials with the exclusion of air.

The solvent used for the oxidizing solution in the spectrometer was Matheson Spectrograde dioxane which could be used directly without purification.

Choice of Solvent and Metal. Dioxane was used frequently because sodium could be dispersed (*ca.* 1-mm diameter) at the boiling point. On occasion the dioxane was removed and replaced with DME or THF. It is also possible to use toluene for the preparation of the dispersion. Potassium globules tend to aggregate readily under most conditions and we generally used sodium metal. Much of our work was done in DME but in retrospect it seems that THF would have been preferable because it is a better solvent for many of these organometallic compounds.

9,10-Diphenylanthracene (DPA). The reaction of excess phenyllithium in ether with anthraquinone followed by reduction of the crude diol with hydriodic acid in boiling acetic acid yields fairly pure DPA. This material or that obtained from commercial sources was purified by passing a methylene chloride solution of the hydrocarbon through a column of Woelm neutral alumina (Activity 1) followed by recrystallization from toluene. DPA was obtained as pale yellow prisms, mp 252–254° (lit.[24] 249–250°).

9,10-Dichloro-9,10-dihydro-9,10-diphenylanthracene (DPACl$_2$). A stream of chlorine gas was bubbled through a stirred solution of DPA (10 g) in methylene chloride (500 ml) for 10 min. The solution was stirred for another 30 min and then evaporated to dryness with a stream of nitrogen under gentle warming. The colorless residue had mp 169–170° dec (lit.[24] 170° dec). Two recrystallizations from methylene chloride–hexane gave colorless crystals (2.5 g) of DPACl$_2$, mp 173–175°. Its solutions had no fluorescence.

Reaction of Potassium with DPA. A solution of DPA (3.3 g, 10 mmoles) in THF (300 ml) was stirred with a dispersion (*ca.* 1-mm diameter) of potassium (0.78 g, 20 mg-atoms). The mixture became dark blue in color immediately. The color changed to dark violet after the solution had been stirred for 20 hr (dianion formation to some extent) but was restored to its original hue by the addition of more DPA (3.3 g, 10 mmoles). In general we treated 1.1 moles of hydrocarbon with 1 mole of metal to avoid complications resulting from the presence of dianion, and we assume that the monoanions do not disproportionate.

Reaction of K$^+$DPA$^-$ with DPACl$_2$. DPA (1.16 g, 4.85 mmoles) was added to a dispersion of potassium (137 mg, 3.52 mg-atoms) in DME (65 ml). The mixture became dark blue in color rapidly. After it had been stirred for 24 hr, the solution was transferred to a dropping funnel. The salt which had precipitated was dissolved in fresh DME and combined with the original solution. The solution of K$^+$DPA$^-$ was then added dropwise to a stirred solution of DPACl$_2$ (700 mg, 1.74 mmoles) in DME (70 ml). There was a flash of light identified visually as DPA fluorescence as each drop hit the surface of the DPACl$_2$ solution. The solution of the chloride, initially colorless, acquired an orange color as the reaction proceeded but was pale yellow after all of the DPA$^-$ solution had been added. The turbid solution was concentrated *in vacuo* to about half its original volume and filtered. The colorless solid thus collected was very soluble in water and is assumed to be KCl. The filtrate was evaporated to give a yellow solid, mp 180–230°, whose infrared spectrum was very similar to that of DPA. A portion of this solid (208 mg) was dissolved in acetic acid (5 ml) containing concentrated hydriodic acid (1 ml), and the solution was boiled for 1 hr. The brown solution was diluted with water (50 ml) and treated with aqueous SO$_2$. Extraction with methylene chloride gave a pale yellow solid (182 mg, 88%) which was identified as DPA by melting point (251–252°) and mixture melting point (251–253°) with authentic DPA.

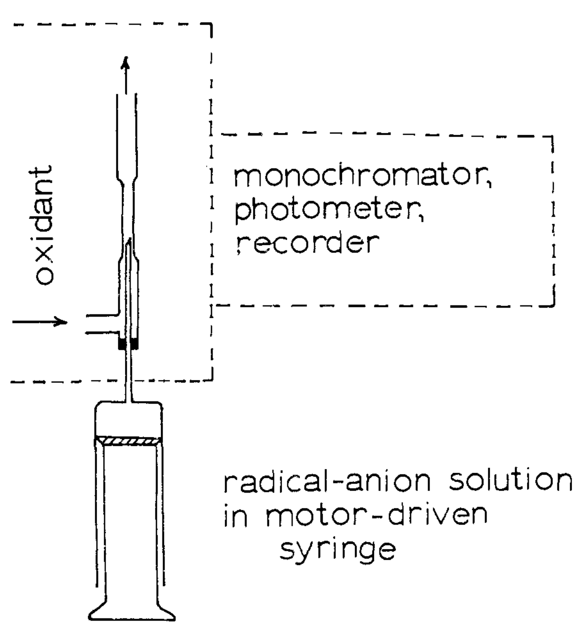

Figure 3. Schematic diagram of the flow-system chemiluminescence spectrometer apparatus.

The chemiluminescence spectrum of this reaction is identical with the normal fluorescence spectrum of DPA (*cf.* Figure 1).

Reaction of K$^+$DPA$^-$ with Benzoyl Peroxides. A solution of K$^+$DPA$^-$ (*ca.* 500 mg, 1.5 mmoles) in THF (50 ml) was added dropwise to a solution of benzoyl peroxide (1.2 g, 5.0 mmoles) in ether (100 ml). DPA fluorescence was observed as each drop of the solution of the anion struck the peroxide solution. After completion of the addition of the anion the turbid yellow solution was evaporated in a stream of nitrogen. A solution of sodium hydroxide in aqueous ethanol was added to the residue and the mixture was stirred for 2.5 hr. After dilution with water the alcohol was removed under reduced pressure at 25°. Extraction with ether yielded a yellow crystalline solid, mp 237–244°, whose infrared spectrum was identical with that of DPA.

The chemiluminescence spectrum of the reaction was recorded in the flow system spectrometer employing a 1% solution (0.04 *M*) of benzoyl peroxide in dioxane and a *ca.* 0.03 *M* solution of K$^+$DPA$^-$ in THF.

The same (visually) light emission was observed upon reaction of K$^+$DAP$^-$ with toluenesulfonyl chloride, methanesulfonyl chloride, oxalyl chloride, toluenesulfonic acid anhydride, and mercuric chloride or aluminum chloride in dioxane or THF solution. No light was visible upon reaction with a solution of commercial lauroyl peroxide, even in a dark room. Di-*t*-butyl peroxide also did not produce any chemiluminescence.

9,10-Dibenzoyloxy-9,10-dihydro-9,10-diphenylanthracene. This procedure is typical of several attempted preparations of pure samples of this compound, none of which gave completely satisfactory material. A mixture of DPACl$_2$ (1.0 g, 2.5 mmoles) and silver benzoate (2.0 g, 8.8 mmoles) in DME (50 ml) was stirred in the dark for 2 weeks. After filtration the solvent was removed under reduced pressure. Crystallization of the oily residue from ether gave a colorless solid (0.30 g), mp 225–230°. The infrared spectrum was consistent with that anticipated and had moderately strong carbonyl absorption at 5.78 μ. *Anal.* Calcd for C$_{40}$H$_{28}$O$_4$: C, 83.90; H, 4.93. Found: C, 84.47, 84.37; H, 5.83, 5.62; Cl, undetectable. The same reaction was carried out in pyridine or dimethylformamide solution and gave products of similar behavior. Pinazzi[25] reports mp 281° with prior decomposition at 250–260° for material prepared by carrying out this reaction in ether for 8 days.

9,10-Diacetoxy-9,10-dihydro-9,10-diphenylanthracene. A mixture of DPACl$_2$ (1.0 g, 2.5 mmoles) and silver acetate (1.7 g, 10 mmoles) in ether (30 ml) was stirred for 2 days in the dark. The insoluble material was collected on a filter and washed with ether.

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[24] C. K. Ingold and P. G. Marshall, *J. Chem. Soc.*, 3080 (1926).

[25] C. Pinazzi, *Ann. Chim.*, 7, 406 (1962).

It was then extracted with hot benzene, and the material thus obtained was crystallized from ethyl acetate to give a colorless solid (0.42 g), mp 260° dec. *Anal.* Calcd for $C_{30}H_{24}O_4$: C, 80.33; H, 5.39. Found: C, 79.48, 5.51; Cl, undetectable. Pinazzi[25] reports mp 222° for material made by this procedure. The infrared spectrum had strong bands at 5.72 and 8.1 μ.

Reaction of N-Methylacridone Ketyl with Benzoyl Peroxide. N-Methylacridone (2.87 g, 13.8 mmoles) was added to DME (300 ml) in which sodium (0.29 g, 13 mg-atoms) had been dispersed. After the mixture had been stirred for 24 hr, there was no unreacted metal discernible in the dark green mixture; some of the ketyl had crystallized from solution. Titrimetric analyses of the supernatant liquid indicated that the concentration of ketyl was 0.0166 *M*. A portion of this solution (200 ml, 3.2 mmoles) was added dropwise to a solution of benzoyl peroxide (0.78 g, 3.2 mmoles) in DME (100 ml). Bright blue chemiluminescence was observed upon mixing. After completion of the addition, aqueous potassium hydroxide solution (100 ml, 5%) was added and the mixture was stirred for 1 hr. Evaporation of the DME under reduced pressure left a solid which was filtered. Its weight (1.0 g; theoretical, 0.68 g) indicated that a considerable amount of unreacted ketone was present in the ketyl solution. The solid was identified as N-methylacridone by melting point, mixture melting point, and infrared spectrum. The aqueous filtrate was brought to pH 8 and extracted with ether in an attempt to isolate phenolic products resulting from bond formation between the ketyl and the peroxide, but only a trace of material was obtained.

The solution of the ketyl gave luminescent reactions with toluenesulfonyl chloride (weaker than benzoyl peroxide) and oxalyl chloride. The luminescence appeared (visually) to be N-methylacridone fluorescence. No light was observed upon reaction with lauroyl peroxide.

The chemiluminescence emission spectrum was determined in the flow spectrometer by injecting a solution of the ketyl (*ca.* 0.01 *M*) into a flowing solution of benzoyl peroxide (2%, 0.08 *M*) in dioxane.

N-Phenylcarbazole. Commercial material was recrystallized from hexane and then from nitromethane and had mp 97–98° (lit.[26] 88–89°). Sublimation (0.01 mm, bath at 90°) gave a colorless solid which had mp 97–98° after crystallization from hexane.

Preparation of the Anion. N-Phenylcarbazole (4.75 g, 51.2 mmoles) was added to a dispersion of potassium metal (1.56 g, 40 mg-atoms) in DME (400 ml). The solution became blue rapidly and the color had not changed its hue after the mixture had been stirred for 20 hr. Some unreacted metal was still visible at this time. The solution was removed with a syringe after the metal had been allowed to settle. It gave a bright blue chemiluminescence upon dropwise addition to solutions of benzoyl peroxide, toluenesulfonyl chloride, or toluenesulfonic acid anhydride, but only a weak luminescence with oxalyl chloride. A very faint reddish light was emitted upon reaction with lauroyl peroxide in DME; it was visible only in a dark room.

Reaction of the N-Phenylcarbazole Anion with *p*-Toluenesulfonyl Chloride. A solution of the anion was prepared from the amine (6.9 g, 28 mmoles) and sodium (0.65 g, 28 mg-atoms) in DME (1 l.). The mixture was stirred for *ca.* 24 hr, and the dark blue supernatant liquid was removed with a syringe. The unreacted sodium metal amounted to 40% of the original quantity. The solution of the anion was added dropwise to a solution of toluenesulfonyl chloride (10.8 g, 56.5 mmoles) in DME (300 ml). Bright blue chemiluminescence was observed as each drop of the anion solution struck the oxidizing solution. After completion of addition the turbid reaction mixture was poured into aqueous sodium hydroxide solution (2 l., 1%) and kept overnight in a refrigerator. Extraction with methylene chloride and thorough removal of the solvent gave a crystalline product whose infrared spectrum was virtually identical with that of N-phenylcarbazole.

Chemiluminescence spectra were obtained by injecting a *ca.* 0.05 *M* solution of the potassium salt of N-phenylcarbazole into a 1% (0.04 *M*) solution of benzoyl peroxide in dioxane, or a 2% (0.1 *M*) solution of toluenesulfonyl chloride in dioxane. The phosphorescence spectrum of N-phenylcarbazole in rigid glassy 2-methyltetrahydrofuran was measured at *ca.* 80°K with an Aminco-Keirs instrument with excitation at 300 mμ. The fluorescence spectrum was measured with the same instrument using deoxygenated solutions of 0.01, 0.1, 1.0 mole/l. in Spectrograde dioxane as well as Nujol and cyclohexane at various concentrations. In addition to the spectrum presented in Figure 2, there was an extremely weak (structureless) fluorescence at about 425 mμ which required excitation at 385 mμ. The spectrum did not change appreciably under the various conditions used for measurement.

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[26] F. D. Hager, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1932, p 547.