interligand $\pi$–$\pi$ overlap is significantly diminished in the octahedral species. Hence, the type of interaction suggested to produce "dithiene resonance" may well be the most important stabilizing factor of the prismatic geometry.

## Semiconducting Properties of Metal Dithienes

The semiconducting properties of the metal dithienes provide another striking example for the far-reaching analogy of the complexes with $\pi$-delocalized organic heterocyclic systems. The conductivity of organic compounds is well known to correlate with the energy difference between the highest occupied and the lowest unoccupied $\pi$ molecular orbitals.[32] Since this energy difference is small in the dithienes, their conductivity is indeed much higher than that of large aromatic compounds, and in some cases even equal to that of charge-transfer complexes.[33]

The present Account on metal dithienes shows that while progress has been made toward the qualitative understanding of the bonding situation, considerable efforts are still necessary to explain finer details of the electronic structures in numerous individual compounds of this type. Will other unsaturated sulfur ligands form transition metal derivatives with dithiene-type properties? On the basis of group theoretical considerations and the distinction of the ligands into "even" and "odd" systems, this author predicted that the chelates of the latter will not possess the unusual chemical properties, stabilities, and structures of the dithienes.[8a] In the meantime sufficient data have become available on transition metal chelates of dithiocarboxylic acids (e.g., dithiobenzoic acid),[34] of 2,4-pentanedithione,[35] and of 1,2-dithiotropolone[36] which indicate that this prediction is probably correct. The metal dithienes thus form a group of compounds whose properties are strongly determined by the topology of the ligands.

(32) For general references see: "Organic Semiconductors," T. T. Brophy and T. W. Buttrey, Ed., The Macmillan Co., New York, N. Y., 1962.
(33) E. J. Rosa and G. N. Schrauzer, *J. Amer. Chem. Soc.*, in press.

(34) (a) J. P. Fackler, Jr., D. Coucouvanis, J. A. Fetchin, and W. C. Seidel, *ibid.*, **90**, 2734 (1968); (b) C. Furlani and M. L. Luciani, *Inorg. Chem.*, **7**, 1586 (1968); (c) M. Bonamico and G. Dessy, *Chem. Commun.*, 483 (1968).
(35) (a) R. L. Martin and I. M. Stewart, *Nature*, **210**, 522 (1966); (b) R. Beckett and B. F. Hoskins, *Chem. Commun.*, 909 (1967).
(36) C. E. Forbes and R. H. Holm, *J. Amer. Chem. Soc.*, **90**, 6884 (1968).

# Chemiluminescence from Concerted Peroxide Decomposition Reactions[1]

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Chemiluminescence, the emission of light from chemical reactions at ordinary temperatures in the absence of flame, has attracted interest since man first became aware of the fireflies and other luminescent organisms in his environment. A variety of reactions, inorganic and organic as well as biochemical, are known to emit light, and although most chemiluminescent reactions are dim and inefficient, chemiluminescence has been the subject of considerable investigation.[2]

In addition to the scientific interest customary for unusual phenomena, chemiluminescence has potential importance as a practical light source. In principle, one molecule of reactant can generate one quantum of light, and in a perfectly efficient process 1 mol of reactant would generate 1 mol of quanta or 1 einstein. It is easily calculated on that basis that 1 lb of perfectly efficient chemiluminescent material might provide 67,000 lumen hr of light, equivalent to the output of a 40-W incandescent bulb operating for 6 days.

This practical potential has stimulated fundamental chemiluminescence research in this laboratory since 1961. Aside from the enzymatic firefly process (approximately 0.88 einstein mol$^{-1}$ or 88%),[3] chemiluminescent reactions known at that time were poorly efficient, providing quantum yields on the order of 1% at best. It was clear that practical chemiluminescence would require a new reaction deliberately designed to accommodate the specific factors inherent to efficiency. This Account surveys certain aspects of an effort to establish efficiency criteria for chemiluminescence.

(2) T. Goto and Y. Kishi, *Angew. Chem. Intern. Ed. Engl.*, **7**, 407 (1968); F. McCapra, *Quart. Rev.* (London), **20**, 485 (1966); K. D. Gundermann, *Angew. Chem. Intern. Ed. Engl.*, **4**, 566 (1965); V. I. Papisova, V. Y. Shlyapintokh, and R. F. Vasl'ev, *Russ. Chem. Rev.*, **34**, 599 (1965); *Photochem. Photobiol.*, **4**, 957 (1965); H. H. Seliger and W. D. McElroy, "Light: Physical and Biological Action," Academic Press, New York, N. Y., 1965; E. J. Bowen, *Pure Appl. Chem.*, **9**, 473 (1964); "Light and Life," W. D. McElroy and B. Glass, Ed., Johns Hopkins Press, Baltimore, Md., 1961; E. N. Harvey, "A History of Luminescence," The American Philosophical Society, Philadelphia, Pa., 1957; H. Eyring, F. P. Johnson, and M. J. Polissar, "The Kinetic Basis for Molecular Biology," John Wiley & Sons, Inc., New York, N. Y., 1954, p 162; A. Zweig, *Advan. Photochem.*, in press.

(3) H. H. Seliger and W. D. McElroy, *Arch. Biochem. Biophys.*, **88**, 136 (1960).

## The General Chemiluminescence Mechanism

Light emission can result from incandescence or luminescence. Incandescence arises from the conversion of vibrational energy to radiant energy and occurs from all objects at temperatures above absolute zero. Luminescence, in contrast, is emission from an electronic excited state. Thus, in fluorescence, the absorption of light in the longest wavelength absorption band of an organic molecule produces the first singlet excited state by promoting an electron from the highest bonding orbital to the lowest antibonding orbital. Reversal of the process after about $10^{-6}$–$10^{-9}$ sec generates a photon and the original ground-state molecule.[4] In chemiluminescence the emission process is identical, but the necessary excited molecule must be produced in a chemical reaction. Thus, in general, a chemiluminescent reaction involves three stages:[5a] (1) preliminary reactions which provide a "key intermediate," (2) an excitation step in which the chemical energy of the key intermediate is converted to electronic excitation energy, and (3) fluorescence emission from the excited reaction product of the excitation step. As in any multistep process the chemiluminescence quantum yield will be the product of the yields of the separate steps, and it is thus not surprising that efficient chemiluminescence is rare. Most reactions do not produce significant yields of excited products, and most excited molecules are not significantly fluorescent.

Identification of the emitting species is obviously critical to chemiluminescence studies and can sometimes be accomplished by matching the fluorescence spectrum of an observed or suspected reaction product with the chemiluminescence spectrum. Unfortunately chemiluminescence spectra often lack uniquely characteristic features, and conclusions can be uncertain. If the emitter can be identified and is stable, its fluorescence quantum yield can be measured independently of the chemiluminescent reaction and the yield of excited product can be determined

yield of excited emitter =

$$\frac{\text{chemiluminescence quantum yield}}{\text{fluorescence quantum yield}}$$

An excitation reaction, particularly a free-radical or one-electron-transfer process in which spin can be conserved, can in principle provide a triplet excited state, and reactions believed to involve triplet emitters are known.[6] Triplet states, however, are inefficient emitters in solution at ordinary temperatures.[7] Efficient chemiluminescence requires the singlet excited state of an efficient fluorescer.[8]

The chemiluminescence investigator is primarily interested in the excitation process, that is, the structure of the key intermediate, the identity of the emitting species, and the excitation mechanism. Chemiluminescent reactions, however, are complex, and the excitation step tends to be obscured by the preliminary steps, by competing nonluminescent side reactions, and by subsequent steps which destroy the initial reaction products. In classical reactions the excitation process may constitute substantially less than a few per cent of the over-all process, so that mechanistic data and product analyses pertinent to the over-all process will not necessarily bear on the chemiluminescence mechanism.

The emitted light, however, bears directly on the chemiluminescent process. The intensity of emission (in einsteins $\text{sec}^{-1}$ $\text{l.}^{-1}$) is the product of the reaction rate and the chemiluminescence quantum yield. Ordinarily both the rate and quantum yield will vary with time during a chemiluminescent reaction so that the intensity will not be related to the reaction kinetics in a simple way. However, if the quantum yield can be maintained constant throughout a reaction, the intensity will be proportional to the reaction rate, and the rate of intensity decrease with time can be related to the concentrations of reactants involved in the rate-determining steps. Factors influencing the quantum yield can then be investigated independently of the kinetics.

This approach has been used to investigate the chemiluminescent reaction of 3-aminophthalhydrazide (1) with potassium persulfate and alkaline hydrogen peroxide.[9] Both quantum yield and rate can change with the reactant concentrations, but a constant quantum yield within an experiment could be achieved by the use of low concentrations of 1 with a large excess of the other reactants. Under these pseudo-first-order conditions, only the concentration of 1 changed significantly during an experiment. Thus, the intensity was directly proportional to the concentration of 1, and the first-order rate equation took the form

$$\ln\left([1^0]/[1]\right) = \ln\left(I^0/I\right) = -kt$$

Plots of log intensity ($I$) vs. time were linear, and the pseudo-first-order rate constant, $k$, was determined from the slope. By varying the concentrations of the other reactants while maintaining a large excess, it was found that $k$ was proportional to the persulfate concentration but independent of pH and hydrogen peroxide concentration. The quantum yield, however, increased with increasing hydrogen peroxide concentration. The essential features of the mechanism

(4) E. J. Bowen and F. Wokes, "Fluorescence of Solutions," Longmans, Green, New York, N. Y., 1953; R. M. Hochstrasser and G. B. Porter, *Quart. Rev.* (London), 14, 146 (1960).

(5) (a) M. M. Rauhut, *et al.*, Technical Report No. 1 to the Office of Naval Research and Advanced Research Projects Agency, AD No. 419-212 (1963) (this series of reports is available from the Clearinghouse for Federal Scientific and Technical Information, Springfield, Va.); (b) No. 2, AD 426-528 (1963); (c) No. 3, AD 435-856 (1964); (d) No. 4, AD 602-272 (1964); (e) No. 5, AD 606-989 (1964); (f) No. 7, AD 460-413 (1965); (g) No. 8, AD 466-061 (1965).
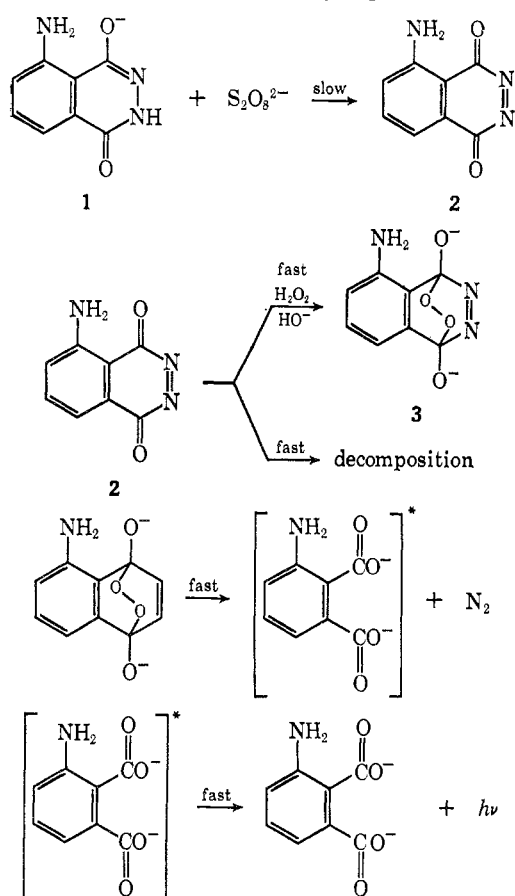
(6) V. Ya. Shlyapintokh, O. N. Karpukhin, L. M. Postnikor, V. F. Tsepalov, A. A. Vichutinskǔ, and I. V. Zakharov, "Chemiluminescence Techniques in Chemical Reactions," Plenum Publishing Corp., New York, N. Y., 1968.

(7) C. A. Parker, *Advan. Photochem.*, 2, 305 (1964).

(8) M. M. Rauhut, D. Sheehan, R. A. Clarke, and A. M. Semsel, *Photochem. Photobiol.*, 4, 1097 (1965).

(9) M. M. Rauhut, A. M. Semsel, and B. G. Roberts, *J. Org. Chem.*, 31, 2431 (1966).

**Chart I**

**3-Aminophthalhydrazide Chemiluminescence in Reaction with
Potassium Persulfate and Hydrogen Peroxide**

tions alone, it would appear that reactions involving a highly exothermic discrete step which directly provides small product molecules having few bonds capable of accepting vibrational energy could have potential for chemiluminescence.

It occurred to me[5a] (and independently to Dr. F. McCapra[11,12]) that certain concerted peroxide decomposition reactions might accommodate the energy requirement and thus provide a basis for efficient chemiluminescence design. For example, experiments by Bartlett and coworkers indicate that the decomposition of $t$-butylperoxyoxalic acid (4) involves concerted bond cleavage,[13] and it is easily shown that concerted decomposition of 4 by a free-radical chain, ionic, or cyclic path would give a $-\Delta F$ of about $-100$ kcal ($\Delta H = \sim -70$ kcal) in a single step.[8] The

$$(CH_3)_3COO\overset{OO}{\underset{\text{4}}{CCOH}} \longrightarrow (CH_3)_3COH + 2CO_2$$
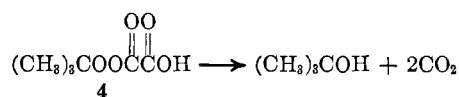
source of the energy is primarily the high free energy of formation of the carbonyl group; in a concerted decomposition of 4, two carbonyl groups would be formed simultaneously.

Such reasoning has led to the design of several new chemiluminescent reactions. McCapra and coworkers[11,12] and our group[5a–g] independently selected the acridine system for initial work because of relatively easy synthesis and the high fluorescence efficiency of N-methylacridone. Both groups investigated the reaction[12,14]

proposed for the reaction are summarized in Chart I. The first step is rate determining, and increasing 1 or persulfate increases the intensity by increasing the rate. Increasing hydrogen peroxide, in contrast, increases the intensity by diverting a larger portion of intermediate 2 to proposed key intermediate 3 in a fast, non-rate-determining step.
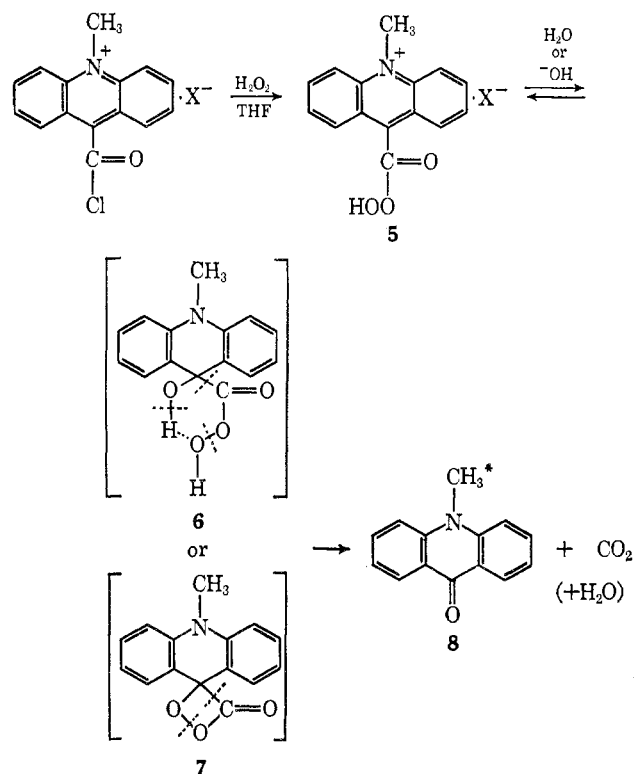
Frequent attempts have been made to investigate chemiluminescence mechanisms by correlating the initial intensity with the initial reactant concentrations. This approach is unsatisfactory, however, because it does not distinguish between rate and quantum yield factors.

## Chemiluminescence from Concerted Peroxide Decomposition Reactions

Excitation of a visible fluorescer requires 41 (700 m$\mu$) to 71 kcal mol$^{-1}$ (400 m$\mu$), and in chemiluminescence this substantial energy must be transferred to the fluorescer in a single reaction step.[8] This critical energy, even if available, can in principle be distributed among the vibrational modes of the product molecules and will not necessarily produce electronic excitation. In addition to energy requirements, factors relating to the probability of crossing between ground-state and excited-state potential energy sufaces should influence the excitation process.[10] But from energy considera-

(10) M. G. Evans, H. Eyring, and J. F. Kincaid, *J. Chem. Phys.* **6,** 349 (1938).

(11) F. McCapra and D. G. Richardson, *Tetrahedron Letters,* **43,** 3167 (1964).

which was found capable of providing quantum yields as high as 3%[5g] under suitable conditions. N-Methyl-acridone (8) and $CO_2$ are the predominant reaction products, and the chemiluminescence spectrum matches the fluorescence spectrum of 8.[12,14] Peroxy acid 5 is stable under strongly acidic conditions; the addition of water or base is necessary to complete the reaction and obtain chemiluminescence.[14] Moreover, the chemiluminescent reaction, once begun by base addition, can be stopped by acidification and restarted by addition of new base. Thus pseudo base 6[14] or cyclic peroxide 7[12] was suggested as a probable intermediate.

Peroxide intermediates 6 and 7 should both be capable of meeting the chemiluminescence energy requirement. The present evidence does not definitively distinguish between them. However, chemiluminescence is still observed when hydrogen peroxide is replaced by t-butyl hydroperoxide or peroxylauric acid. Thus structures 9 and 10, analogous to 6, are evidently capable of chemiluminescent decomposition,[14] and it appears that 7 is not essential.

**9**  **10**  **11**
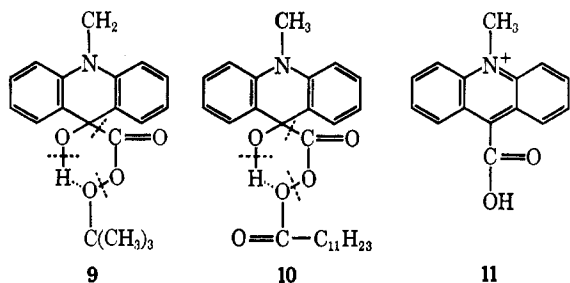
Water, moreover, appears to be specifically required for chemiluminescence. Dilution of solutions containing 5 with water generates light, while dilution with ethanol or tetrahydrofuran does not.[14] Water would be required for the formation of 6, but not 7. Thus both the requirement of water for chemiluminescence and the observation of chemiluminescence from organic hydroperoxides would appear to indicate that 6 rather than 7 is involved. It has been argued, alternatively, that chemiluminescence from 7 might require a specific hydration.[12]

The reaction is not a free-radical chain process since the free-radical inhibitor 4-methyl-2,6-di-t-butylphenol is without effect.[5g] Decomposition of 6 would thus appear to involve an ionic process or a cyclic transition state, and since the reaction can occur under weakly acidic conditions the latter appears more likely. Reaction of 9-carboxy-N-methylacridinium chloride (11) with alkaline hydrogen peroxide also gives 8 plus $CO_2$ rapidly and quantitatively, but the reaction is not chemiluminescent.[14] Thus, the peroxycarbonyl struc-

**Chart II**
**Tentative Mechanism for Oxalyl Chloride Chemiluminescence**
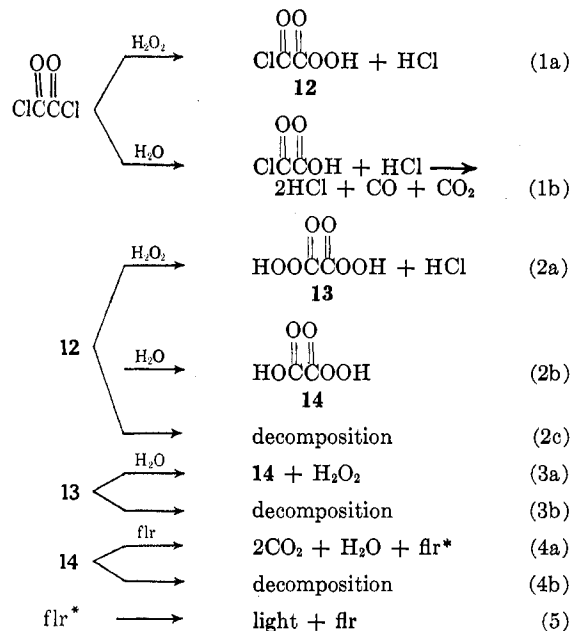
ture is required for chemiluminescence in this series, and the essential character of intermediates 6 or 7 is further indicated.

Recent studies indicate that the simultaneous formation of two carbonyl groups by concerted peroxide decomposition accounts well for the more efficient classical chemiluminescent reactions.[8,9,15−17] Several new chemiluminescent reactions believed to involve the concerted cleavage of four-membered cyclic peroxides have been reported.[18,19]

## Peroxyoxalate Chemiluminescence

Chemiluminescence is obtained from the reaction of oxalyl chloride, hydrogen peroxide, and a fluorescent compound such as anthracene.[20] Although the reaction, as reported, is poorly efficient, its apparent simplicity encouraged our group to select it for detailed mechanism studies. In contrast to our expectations, the reaction was found to be capable of relatively high quantum yields (on the order of 5%) under suitable conditions, while the mechanism is complex.[21] The proposed mechanism (Chart II) involves four series of competitive reactions, followed by the emission process, step 5. Steps a in each series along with step 5 were suggested to constitute the

(12) F. McCapra, D. G. Richardson, and Y. C. Chang, Photochem. Photobiol., 4, 1111 (1965).

(13) P. D. Bartlett and R. E. Pincock, J. Am. Chem. Soc., 82, 1769 (1960); P. D. Bartlett in "Peroxide Reaction Mechanisms," J. O. Edwards, Ed., Interscience Publishers, New York, N. Y., 1962, p 1.

(14) M. M. Rauhut, D. Sheehan, R. A. Clarke, B. G. Roberts, and A. M. Semsel, J. Org. Chem., 30, 3587 (1965).

(15) E. H. White, O. Zafiriou, H. H. Kagi, and J. H. M. Hill, J. Am. Chem. Soc., 86, 940 (1964); E. H. White and M. M. Bursey, ibid., 86, 941 (1964).

(16) G. Sonnenberg and D. M. White, ibid., 86, 5685 (1964).

(17) E. H. White and M. J. C. Harding, ibid., 86, 5686 (1964); F. McCapra and Y. C. Chang, Chem. Commun., 522 (1966).

(18) T. A. Hopkins, H. H. Seliger, E. H. White, and M. W. Cass, J. Am. Chem. Soc., 89, 7148 (1967); F. McCapra, Y. C. Chang, and V. P. Francois, Chem. Commun., 22 (1968).

(19) F. McCapra and Y. C. Chang, ibid., 1011 (1967).

(20) E. A. Chandross, Tetrahedron Letters, 761 (1963).

(21) M. M. Rauhut, B. G. Roberts, and A. M. Semsel, J. Am. Chem. Soc., 88, 3604 (1966).

chemiluminescence process, while the competitive reactions in each series reduced the quantum yield by diverting essential chemiluminescence intermediates.

Step 5 is firmly established; a wide variety of organic fluorescers may be employed, and for each the spectral distribution of chemiluminescence matches the fluorescence spectrum.
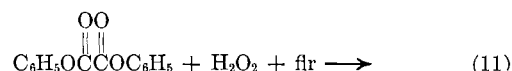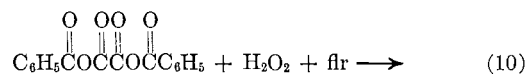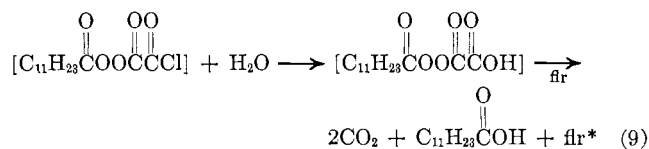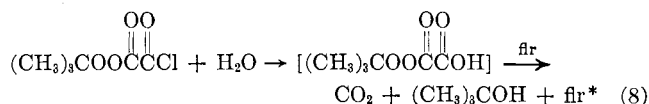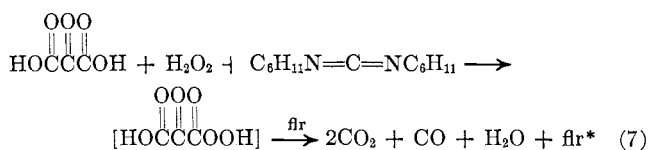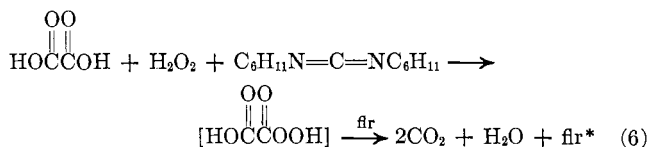
Steps 1a and 1b are the expected rapid nucleophilic substitution reactions of oxalyl chloride with $H_2O_2$ and water. The reaction with water is not chemiluminescent and gives CO and $CO_2$ essentially instantaneously.[22] Series 2 was suggested to account for the observed increase in quantum yield with increasing hydrogen peroxide. In step 3a an acid-catalyzed reaction of diperoxyoxalic acid (13) with water was suggested to give monoperoxyoxalic acid (14) in competition with a nonchemiluminescent decomposition of 13 (step 3b), in order to account for a substantial increase in quantum yield when small amounts of water are added to ethereal reaction solutions.[23] In contrast, quantum yields are reduced when ethanol is added to ethereal reaction mixtures, indicting that an intermediate specifically derived from water is required for chemiluminescence. In series 4 monoperoxyoxalic acid (14) was suggested to be the key intermediate which reacts with the fluorescer in the excitation step. Decomposition of 14 in the absence of fluorescer (step 4b) was suggested to compete with excitation to account for an increase in quantum yield with increasing fluorescer concentration.

Chemiluminescent reactions under pseudo-first-order conditions in ether solution provided linear plots of log intensity vs. time. With oxalyl chloride as the limiting reactant, pseudo-first-order rate constants were independent of oxalyl chloride, $H_2O_2$, and fluorescer concentrations, showing that the latter two reactants were not involved in rate-determining steps. In contrast, the reaction rate as well as the quantum yield increased with increasing water concentration, suggesting that series 3 in the mechanism was rate determining. This could be true only if steps 1 and 2 were essentially complete prior to the bulk of light emission. It was shown by infrared spectral analyses that the disappearance of chlorocarbonyl species from the system was indeed rapid relative to the rate of intensity decay.

Interest in chemiluminescence mechanisms focuses on the excitation step. This is particularly so for oxalyl chloride chemiluminescence because, in spite of a multiplicity of competing nonchemiluminescent side reactions, the quantum yield can approach 5%. The excitation step must thus have a high inherent

efficiency. If step 4a correctly indicates the excitation process, it is clear that one need not use oxalyl chloride to achieve efficient chemiluminescence; only a peroxyoxalate such as 14 which is capable of concerted decomposition need be generated as a high-yield intermediate, and in principle a number of starting materials might serve this purpose.

Initial attempts to discover other examples of peroxyoxalate chemiluminescence met with only limited success. Reactions 6–9 were found to be chemiluminescent,[8] but reactions 10 and 11 gave very little light, even though all might be expected to provide active peroxyoxalate intermediates.

$$HOCCOH + H_2O_2 + C_6H_{11}N{=}C{=}NC_6H_{11} \longrightarrow$$
$$[HOCCOOH] \xrightarrow{\text{flr}} 2CO_2 + H_2O + flr^* \quad (6)$$

$$HOCCCOH + H_2O_2 + C_6H_{11}N{=}C{=}NC_6H_{11} \longrightarrow$$
$$[HOCCCOOH] \xrightarrow{\text{flr}} 2CO_2 + CO + H_2O + flr^* \quad (7)$$

$$(CH_3)_3COOCCCl + H_2O \rightarrow [(CH_3)_3COOCCOH] \xrightarrow{\text{flr}}$$
$$CO_2 + (CH_3)_3COH + flr^* \quad (8)$$

$$[C_{11}H_{23}COOCCCl] + H_2O \longrightarrow [C_{11}H_{23}COOCCOH] \xrightarrow{\text{flr}}$$
$$2CO_2 + C_{11}H_{23}COH + flr^* \quad (9)$$

$$C_6H_5COCCOCC_6H_5 + H_2O_2 + flr \longrightarrow \quad (10)$$

$$C_6H_5OCCOC_6H_5 + H_2O_2 + flr \longrightarrow \quad (11)$$

Continued investigations of reactions related to (10) and (11), however, provided a series of remarkable chemiluminescent reactions illustrated by eq 12–18. (In these equations DPA is 9,10-diphenylanthracene, and BPEA is 9,10-bis(phenylethynyl)anthracene. Maximum reported quantum yields in $10^2$ einsteins $mol^{-1}$ are indicated in parentheses.)

In each reaction the light is derived from the first singlet excited state of the fluorescer, and a variety of fluorescers may be used to provide a range of colors. Since the fluorescer is not normally consumed, the fluorescer concentration may be substantially less than stoichiometric. Efficient chemiluminescence requires that the starting oxalate have a high order of reactivity toward hydrogen peroxide; this accounts in part for the variation in maximum reported quantum yields and for the absence of strong luminescence from re-

$$(C_6H_5)_3CCOCCOCC(C_6H_5)_3 + H_2O_2 + DPA \longrightarrow$$
$$\text{light (13\%)} \quad (12)^{25}$$
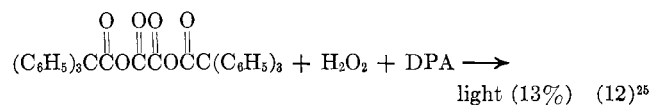
(22) H. Staudinger, Ber., 41, 3558 (1908).

(23) Step 3b appears to be important only in ethereal media, since the effect of water is much less pronounced in dimethyl phthalate. Substantially higher quantum yields, moreover, were obtained in dimethyl phthalate, indicating an ether-caused nonchemiluminescent side reaction. Step 3b in ether solution was thus suggested to involve an ether-induced free-radical chain reaction, well known for other peroxides.[24]

(24) K. Nozaki and P. D. Bartlett, J. Am. Chem. Soc., 68, 1686 (1946).

(25) L. J. Bollyky, R. H. Whitman, B. G. Roberts, and M. M. Rauhut, ibid., 89, 6523 (1967).

$$\text{(NO}_2\text{-aryl)} - O - \overset{O\,O}{\underset{}{CC}} - O - \text{(aryl-NO}_2\text{)} + H_2O_2 +$$

$$\text{rubrene} \longrightarrow \text{light} \quad (23\%) \quad (13)[26]$$

$$\text{(Cl-aryl)} - O - \overset{O\,O}{\underset{}{CC}} - O - \text{(aryl-Cl)} + H_2O_2 +$$

$$\text{rubrene} \xrightarrow{\text{base}} \text{light} \quad (18\%) \quad (14)[27]$$

$$(CF_3)_2CHO\overset{O\,O}{\underset{}{CC}}OCH(CF_3)_2 + H_2O_2 + \text{BPEA} \xrightarrow{\text{base}}$$

$$\text{light} \quad (1.8\%) \quad (15)[27]$$

$$\text{(phthalimide)} N O\overset{O}{\underset{}{C}}\overset{O}{\underset{}{C}} ON \text{(phthalimide)} + H_2O_2 + \text{DPA} \longrightarrow$$

$$\text{light} \quad (8.7\%) \quad (16)[28]$$

$$\text{(benzimidazole)} N \overset{O\,O}{\underset{}{CC}} N \text{(benzimidazole)} + H_2O_2 + \text{DPA} \xrightarrow{\text{base}}$$

$$\text{light} \quad (1\%) \quad (17)[29]$$

$$\text{(pyridone)} N - \overset{O\,O}{\underset{}{CC}} - N \text{(pyridone)} + H_2O_2 +$$

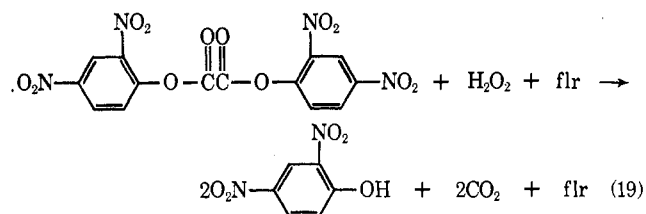$$\text{rubrene} \xrightarrow{\text{acid}} \text{light} \quad (16\%) \quad (18)[30]$$
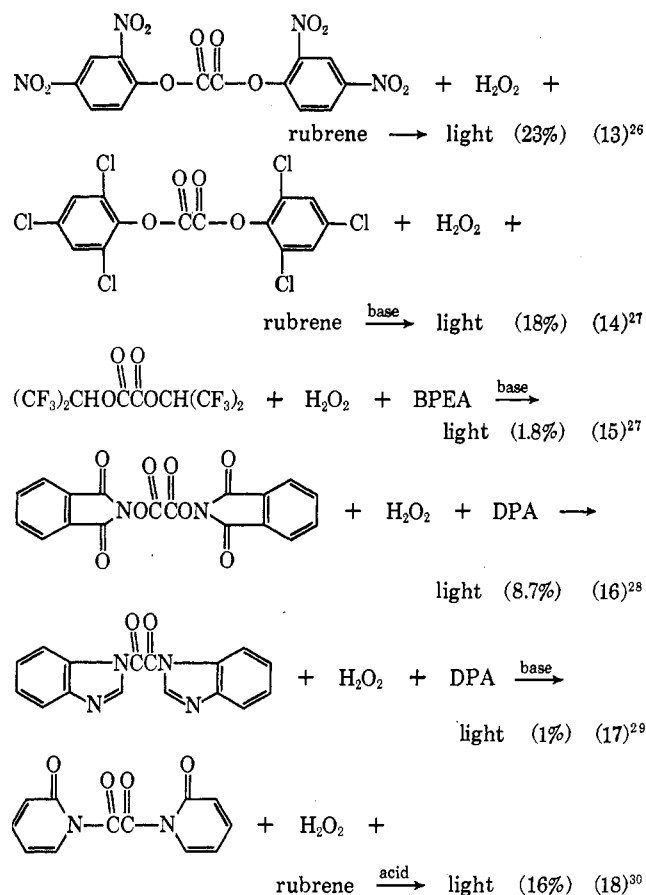
action 11. Most of the reactions are accelerated by base, and base catalysis substantially increases the efficiency of less reactive oxalates. Reaction 18, however, requires acid catalysis for high efficiency.[30]

Oxalate ester chemiluminescent reactions have been investigated in greatest detail to date.[26] The over-all reaction, in a representative case, proceeds according to eq 19. Carbon monoxide and oxygen are also found

$$O_2N\text{-aryl} - O - \overset{O\,O}{\underset{}{CC}} - O - \text{aryl-NO}_2 + H_2O_2 + \text{flr} \longrightarrow$$

$$2 O_2N\text{-aryl} - OH + 2CO_2 + \text{flr} \quad (19)$$

in small amounts but are excluded as chemiluminescent reaction products since their yields are substantially less than the yield of excited state under near optimum conditions. A possible mechanism for the reaction, somewhat modified from the original proposal,[26] is shown in Chart III.

(26) M. M. Rauhut, L. J. Bollyky, B. G. Roberts, M. Loy, R. H. Whitman, A. V. Iannotta, A. M. Semsel, and R. A. Clarke, *J. Am. Chem. Soc.*, **89**, 6515 (1967).
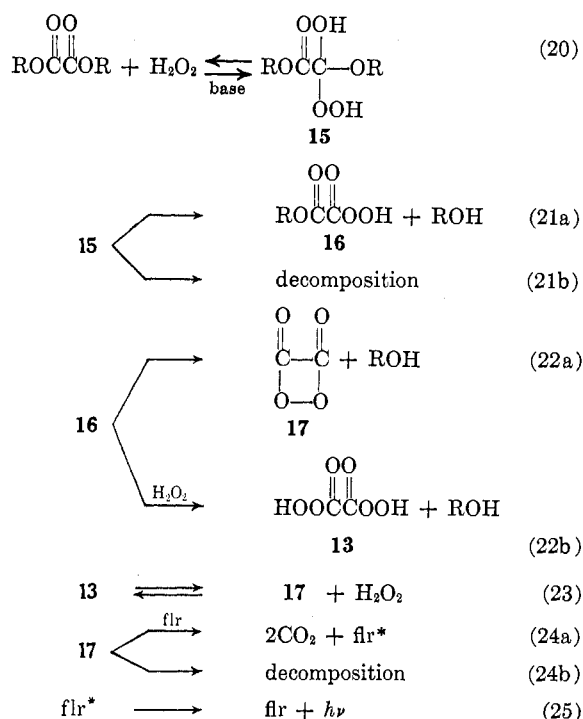(27) L. J. Bollyky, R. H. Whitman, B. G. Roberts, and M. M. Rauhut, unpublished work.
(28) L. J. Bollyky, R. H. Whitman, and B. G. Roberts, *J. Org. Chem.*, **33**, 4266 (1968).
(29) D. R. Maulding, R. A. Clarke, B. G. Roberts, and M. M. Rauhut, *ibid.*, **33**, 250 (1968).
(30) L. J. Bollyky, B. G. Roberts, R. H. Whitman, and J. E. Lancaster, *ibid.*, in press.

**Chart III**
**Tentative Mechanism for Oxalic Ester Chemiluminescence**

$$RO\overset{O\,O}{\underset{}{CC}}OR + H_2O_2 \underset{\text{base}}{\rightleftharpoons} RO\overset{OOH}{\underset{OOH}{C}}\overset{O}{\underset{}{C}}-OR \quad (20)$$

$$\mathbf{15}$$

$$\mathbf{15} \begin{cases} \longrightarrow RO\overset{O\,O}{\underset{}{CC}}OOH + ROH & (21a) \\ & \mathbf{16} \\ \longrightarrow \text{decomposition} & (21b) \end{cases}$$

$$\mathbf{16} \begin{cases} \longrightarrow \overset{O\quad O}{\underset{O-O}{C-C}} + ROH & (22a) \\ & \mathbf{17} \\ \xrightarrow{H_2O_2} HOO\overset{O\,O}{\underset{}{CC}}OOH + ROH & (22b) \\ & \mathbf{13} \end{cases}$$

$$\mathbf{13} \rightleftharpoons \mathbf{17} + H_2O_2 \quad (23)$$

$$\mathbf{17} \begin{cases} \xrightarrow{\text{flr}} 2CO_2 + \text{flr*} & (24a) \\ \longrightarrow \text{decomposition} & (24b) \end{cases}$$

$$\text{flr*} \longrightarrow \text{flr} + h\nu \quad (25)$$

Step 20 is the base-catalyzed nucleophilic addition of hydrogen peroxide to ester carbonyl, known to be rapid with electronegatively substituted aryl acetates.[31] Tetrahedral intermediate **15** would be expected to have momentary existence by analogy to ester hydrolysis mechanisms.[32] Intermediate **15** might decompose (21b) analogously to the decomposition of **18**, suggested by Millburn and Taube,[33] or could undergo the normal elimination of ROH to give peroxyacid **16** (21a). The

$$HO\overset{O}{\underset{}{C}}-\overset{OH}{\underset{OOH}{C}}-OH \longrightarrow 2H_2CO_3$$

$$\mathbf{18}$$
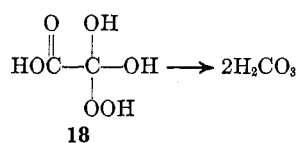
relative rates of steps 21a and 21b would depend in part on the activity of the leaving group in step 21a. Thus step 21a would become faster as the acidity of ROH increased, and the greater fraction of **15** converted to **16** would increase the quantum yield. Competitive steps 21a and 21b thus account for the higher quantum yields obtained from electronegatively substituted oxalates.

Intermediate **16** could undergo intramolecular nucleophilic displacement to give 1,2-dioxetanedione (**17**; step 22a) or react further with hydrogen peroxide to give diperoxyoxalic acid (**13**; step 22b). The evidence suggests that steps 22a and 22b can both lead to chemiluminescence. The over-all stoichiometry of the re-

(31) W. P. Jencks, *J. Am. Chem. Soc.*, **80**, 4585 (1958).
(32) S. L. Johnson, *Advan. Phys. Org. Chem.*, **5**, 237 (1967).
(33) R. M. Millburn and H. Taube, *J. Am. Chem. Soc.*, **81**, 3515 (1959).
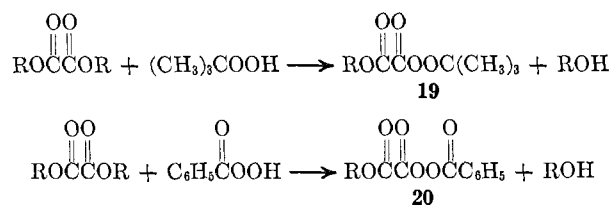
action was found by infrared analysis to be 1:1 $H_2O_2$–oxalate. Moreover, the chemiluminescence quantum yield based on a 1:1 stoichiometry was unchanged with varying $H_2O_2$–oxalate ratio, showing that the chemiluminescence reaction has the same stoichiometry as the over-all process. The 1:1 stoichiometry indicates that **13**, which requires a 2:1 stoichiometry, is not an essential intermediate and that an intermediate such as **17** can lead directly to chemiluminescence. The formation of diperoxyoxalic acid (**13**) would be expected at high $H_2O_2$ ratios, however, and the unchanged quantum yield suggests that **13** can also provide the key chemiluminescent intermediate, as in step 23. Intermediates **13**, **16**, and **17** are, in principle, capable of reacting with water to give monoperoxyoxalic acid, the key intermediate suggested for oxalyl chloride chemiluminescence. Quantum yields and reaction rates of oxalic ester reactions are insensitive to small concentrations of water, however, and although participation by monoperoxyoxalic acid has not been definitely excluded, it appears unlikely.

Other experiments also indicate that the key chemiluminescent intermediate is derived from a 1:1 $H_2O_2$–oxalate stoichiometry. The reaction of equimolar quantities of bis(3-trifluoromethyl-4-nitrophenyl) oxalate (TFMNPO) and hydrogen peroxide in triethyl phosphate containing the fluorescer 9,10-bis(phenylethynyl)anthracene (BPEA) and a trace of basic catalyst provided the bulk of light emission within 6 min and a quantum yield of 5%. In the absence of fluorescer light was not produced, but infrared analysis established that within 6 min all of the TFMNPO had been consumed. Nevertheless, addition of BPEA to the solution at that late stage of the reaction caused emission of the original light yield.[34] Similar results were obtained using an excess of $H_2O_2$ and fluorescer delay periods up to 2 hr.[26] It is clear that a metastable intermediate is formed in the absence of fluorescer and that the fluorescer catalyzes a reaction of the intermediate which leads to chemiluminescence.

Prior to fluorescer addition in these experiments, an effort was made to detect intermediates by infrared spectroscopy. Carbonyl absorption bands corresponding to **16**, **17**, or **13** should be discernible under the conditions used, but aside from $CO_2$, no carbonyl absorption was seen. It may be that such intermediates are unstable under the conditions of the infrared analysis, and experiments are continuing to resolve this point.

While the experiments above are in agreement with monoperoxyoxalic acid (**16**) as a chemiluminescent intermediate, this does not appear to be the intermediate responsible for fluorescer excitation. First, decomposition of **16** would be expected to give $CO_2$ and CO in equal amounts, and CO has been excluded as a product of the chemiluminescent reaction. Second, $H_2O_2$ was found to be specifically required for high quantum yields. Chemiluminescence was approximately 1000-fold less efficient when $H_2O_2$ was replaced

by t-butyl hydroperoxide or peroxybenzoic acid.[26] Thus intermediates **19** and **20**, while analogous to **16**, provide only weak chemiluminescence in contrast.

$$\underset{\text{ROCCOR}}{\overset{\text{OO}}{\parallel\parallel}} + (CH_3)_3COOH \longrightarrow \underset{\textbf{19}}{\overset{\text{OO}}{\underset{\text{ROCCOOC(CH}_3)_3}{\parallel\parallel}}} + ROH$$

$$\underset{\text{ROCCOR}}{\overset{\text{OO}}{\parallel\parallel}} + C_6H_5COOH \longrightarrow \underset{\textbf{20}}{\overset{\text{OO}\quad\text{O}}{\underset{\text{ROCCOOCC}_6H_5}{\parallel\parallel\;\parallel}}} + ROH$$

Finally, reaction of an active oxalate such as bis-(2,4-dinitrophenyl) oxalate (DNPO) with $H_2O_2$ in the absence of fluorescer can be carried out in an evacuated system in which, suspended well above the reaction mixture, is a pad moistened with a fluorescer solution. The reaction solution is not luminescent, but the fluorescent pad lights brightly.[34] The bulk of gas produced, according to infrared analysis, is $CO_2$, indicating that the yield of intermediate is low or that the intermediate is unstable under the conditions of the experiment. But it is clear that a volatile chemiluminescent intermediate is formed, and **16** would not be expected to be volatile. Cyclic intermediate **17** was thus suggested as the intermediate responsible for fluorescer excitation. This proposal accounts for the chemiluminescence stoichiometry, the reaction products, the absence of efficient chemiluminescence from **19** and **20**, which although similar to **16** cannot provide **17**, and the observation of a volatile chemiluminescent intermediate.[26]

Oxalate ester reactions are base catalyzed; even $10^{-4}$ $M$ concentrations of a weak base such as sodium salicylate cause a pronounced acceleration of the light decay rate. Steps 20, 22a, 22b, and 23 all involve nucleophilic reactions of hydroperoxides and should be subject to base catalysis. The available kinetic evidence is not yet sufficient to determine which of these steps are rate determining.

Inasmuch as the reaction rate is independent of the fluorescer concentration under base-catalyzed conditions, step 24 is fast relative to the preceding steps. Increasing fluorescer increases the quantum yield, however, indicating a dark reaction (24b) competitive with the excitation process (24a). An investigation of the effect of fluorescer structure will be reported shortly, in which the variation of quantum yield with fluorescer concentration was determined for more than 20 fluorescers.[35] The competitive processes proposed in step 24 of the mechanism require that a plot of the reciprocal of the quantum yield vs. the reciprocal of the fluoroescer concentration ($F$) be linear according to the equation below, where $Y$ is the product of the yield of the key intermediate **17**, the yield of step 24a, and the fluorescence yield of the fluorescer in step 25.[36]

$$1/Q = 1/Y + (k_{24b}/Yk_{24a})(1/F)$$

(34) M. M. Rauhut and L. J. Bollyky, unpublished work. See ref 26.

(35) M. M. Rauhut, B. G. Roberts, and D. R. Maulding, unpublished work.
(36) See ref 21.

Reciprocal plots of the data were found to be linear, and $Y$ and $k_{24a}/k_{24b}$ could be obtained from the intercept and slope. Since the rate of $k_{24b}$ is assumed to be independent of the fluorescer, the relative rates of the excitation step (24a) for various fluorescers can be determined from the $k_{24a}/k_{24b}$ values.

In general, although there were a few exceptions, the rate of excitation increased as the ionization potential and excitation energy of the fluorescer decreased. It has been suggested that the excitation step involves initial formation of a charge-transfer complex between the intermediate and the fluorescer wherein the fluorescer acts as an electron donor.[26] If this is correct, the rate of excitation would increase as the ionization potential of the fluorescer decreased, in agreement with the experimental results.

As discussed earlier, the over-all yield of excited fluorescer can be determined by dividing the chemiluminescence quantum yield by the fluorescence quantum yield of the fluorescer. Thus $Y$ divided by the appropriate fluorescence quantum yield gives, according to Chart III, the yield of 17 times the yield of excited fluorescer from 17 in step 24a. Since the yield of 17 should be independent of the fluorescer, the relative excitation yields in step 24a could be determined from the $Y$ and fluorescence quantum yield values as a function of fluorescer structure. In general, the excitation yield was found to increase as the excitation energy of the fluorescer decreased. The result is thus in agreement with Eyring's suggestion that decreasing electronic excitation energy should favor the formation of electronic vs. vibrational excited states.[10] With low-energy fluorescers the over-all yield of excited fluorescer was found to approach 60%.

The experiments require that the fluorescer act as a catalyst for decomposition of the chemiluminescent intermediate. It has been suggested that a spontaneous concerted decomposition of 17 might be slow because of the low probability of a reaction which requires the conversion of substantial chemical energy to vibrational energy in small product molecules.[26] The fluorescer would then act as a catalyst by providing an energy acceptor. It should be noted, however, that concerted decomposition of a four-membered ring system such as 17 would be required to provide an excited product if it obeyed the Woodward–Hoffmann symmetry rule.[37,38] Excited singlet $CO_2$ requires an enthalpy change of 110 kcal or more[39] and the formation of two excited triplets (formation of a triplet pair would be required for spin conservation) would require at least as much. Thus concerted decomposition in conjunction with a fluorescer requiring 70 kcal $mol^{-1}$ or less for excitation would be favored. Indeed decomposition of a charge-transfer complex between 17 and a fluorescer could provide a short-lived carbon dioxide–fluorescer mixed eximer[7] capable of dissociation to ground-state $CO_2$ and excited fluorescer.[21]

Our understanding of chemiluminescence remains incomplete, and it is likely that current mechanism proposals will require modification as further evidence becomes available. Current theories, however, have now made possible the successful design of new chemiluminescent reactions. Moreover, peroxyoxalate chemiluminescence has demonstrated that efficient nonenzymatic chemiluminescent reactions are possible.

(37) R. Hoffmann and R. B. Woodward, J. Am. Chem. Soc., 87, 2046 (1965); P. D. Bartlett, Science, 159, 833 (1968).

(38) F. McCapra, Chem. Commun., 155 (1968), has also suggested recently that the Woodward–Hoffmann rule may account for chemiluminescent reactions involving the decomposition of four-membered cyclic species.

(39) M. A. A. Clyne and B. A. Thrush, Proc. Roy. Soc. (London), A269, 404 (1962).

# Ions and Ion Pairs

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While free ions are well known to all chemists, familiarity with ion pairs is less common. The concept of ion pair was introduced by Bjerrum[1] to account for the behavior of ionophores in solvents of low dielectric constant. Ionophores[2] are substances composed of ions which do not combine into covalently bonded molecules. What are, therefore, ion pairs? These were visualized as associates of two oppositely charged ions retaining their basic properties when bonded together by Coulombic forces and, to a lesser extent, by other interactions. Their electric neutrality makes them nonconducting and this was of paramount importance for Bjerrum.

The subject of ion pairs has been reviewed recently by this writer.[3] It was shown that the utility of this concept is lost when one deals with dense systems at elevated temperatures; e.g., it is unprofitable, and perhaps meaningless, to describe molten sodium chloride in terms of free ions and ion pairs. In dilute systems such a description is advantageous since the ions are either far apart from each other or coupled into pairs,

(1) N. Bjerrum, Kgl. Danske Videnskab Selskab, 7, No. 9 (1926).

(2) R. M. Fuoss, J. Chem. Educ., 32, 527 (1955).

(3) M. Szwarc, "Carbanions, Living Polymers and Electron-Transfer Processes," Interscience Publishers, New York, N. Y., 1968.