An Investigation of the Mechanism of Some Electrochemiluminescent Processes[1]

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Abstract: Double-potential-step experiments and spectroscopic measurements, including quantum yield and additive studies, have been made on isobenzofurans and other electrochemiluminescent substances. Preannihilative emission is commonly observable on oxidation of stable anion radicals and reduction of stable cation radicals of fluorescent compounds. A discussion of the possible intermediacy of triplets, impurities, or ion-radical aggregates in this emission process is given. The results for the subject compounds best fit the last of these.

A remarkable number of organic compounds luminesce when subjected to consecutive oxidation–reduction (or reduction–oxidation) at inert electrodes in polar aprotic solvents. This process has been termed electrochemiluminescence (ecl). In many instances, though not always, the emission under such conditions is identical with that of the solution fluorescence emission of the electroactive organic compound. In these instances the electrochemical treatment has served to produce neutral molecules in their first excited singlet state.

Although it is convenient to describe the over-all process in terms of generating the fluorescer cation and anion radicals, followed by annihilation which results in direct generation of the excited singlet, much evidence for other pathways has been uncovered. For example, some systems are found to emit a characteristic fluorescence spectrum even though one of the ion radicals generated has no detectable lifetime in the medium employed.[2] Even more striking is the observation that some stable anion and cation radicals can be oxidized and reduced at overpotentials which are insufficient to produce the counterion, and yet again emission with a characteristic fluorescence spectrum results.[3] The thermodynamic driving force available under these preannihilative conditions is insufficient to provide enough energy to raise the emitting molecule to its first excited singlet in a monomolecular process. Finally, it should be mentioned that in some instances the process of generating an unstable ion radical can result in emission.[4]

We wish to report here on some results which bear on the mechanism by which electronically excited states are reached in electrochemical processes. Included in this investigation are (1) emission studies under double-potential, step-controlled potential conditions; (2) spectroscopic studies of electrochemical emission and also of the light-induced emission from the same molecules; (3) the effect of additives on emission characteristics; (4) studies of the efficiency of the electrochemiluminescence process. This report deals only with systems whose emission under electrochemical stimulation is identical with their fluorescence emission under the same conditions of temperature and solution. Aryl-substituted isobenzofurans and isoindoles were most extensively examined particularly because of their rather bright emission under varying conditions of electrochemical stimulation.

Results

Double-Potential-Step Experiments. In these studies the anion (or cation) was generated at a platinum electrode in a 10^{-3} *M* solution of the fluorescer in N,N-dimethylformamide (DMF) which was 0.1 *M* in the supporting electrolyte, tetra-*n*-butylammonium perchlorate. In the initial step the anion (or cation) was generated for 5 sec at a potential slightly more negative (or positive) that its half-wave potential, and then the potential at the electrode was switched to various positive (or negative) values for the second step. The light output was visually observed but was also measured by a photomultiplier 0.2 sec after initiation of the second step of this double-potential-step experiment. With the isobenzofurans and isoindoles, no emission could be detected by simply generating either ion in deaerated systems, nor was emission detected on the second step, if the voltage of the first step was insufficient to make the ion. The cyclic voltammograms and the potential *vs.* light output curves for 1,3,4,7-tetraphenylisobenzofuran and 1,3,5,6-tetraphenylisobenzofuran are shown in Figure 1. As seen from the figure, 1,3,4,7-tetraphenylisobenzofuran has a relatively stable anion. It also has a dianion and cation which are less stable but still easily detectable on current reversal at the scan rate employed. The cyclic voltammogram of 1,3,5,6-tetraphenylisobenzofuran, however, shows no detectable reduction current for the cation at the fastest scan rate employed (20 V/sec) although the monoanion is apparently quite stable.

The threshold voltages for detection of light from oxidation of anions or reduction of cations are shown in Table I. These voltages were approached from both sides in 0.1-V increments with 0.01-V increments being used as the boundary conditions were established. Since at very low light levels the dark-adapted eye is more sensitive than a photomultiplier,[5] the threshold

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[1] A preliminary communication regarding a portion of this work has appeared: A. Zweig, A. K. Hoffmann, D. L. Maricle, and A. Maurer, *Chem. Commun.*, 106 (1967).

[2] A. Zweig, G. Metzler, A. Maurer, and B. G. Roberts, *J. Am. Chem. Soc.*, **88**, 2864 (1966); **89**, 4091 (1967).

[3] D. L. Maricle and A. Maurer, *ibid.*, **89**, 188 (1967).

[4] D. M. Hercules, R. C. Lansbury, and D. K. Roe, *ibid.*, **88**, 4578 (1966).

[5] For a discussion of the light sensitivity of the eye, *cf.* H. B. Barlow in "Photophysiology," A. C. Giese, Ed., Academic Press Inc., New York, N. Y., 1964, p 163.

Table I. Threshold Overvoltages for Electrochemiluminescence

Compound	Redn potential,[a] V	Threshold oxidative overvoltage,[b] V	Oxidn potential,[c] V	Threshold reductive overvoltage,[b] V
1,3,4,7-Tetraphenylisobenzofuran	−1.86	1.78	+0.89	1.73
1,3,5,6-Tetraphenylisobenzofuran	−1.79[d]	1.49	+0.85[d]	No ecl
1,3-Di-*p*-anisyl-4,7-diphenylisobenzofuran	−1.92	1.26	+0.84	2.18
N-Methyl-1,3,4,7-tetraphenylisoindole	−2.35	1.59	+0.67	2.12
N-Methyl-1,3-di-*p*-anisyl-4,7-diphenylisoindole	−2.42	No ecl	+0.59	2.18
Tetracene	−1.58	1.97–1.93	+0.77	No ecl
Tetracene-5,12-quinone	−1.02	No ecl	+1.75	No ecl

[a] Half-wave potentials *vs.* sce at a dropping Hg electrode in DMF solution. [b] The increment between the half-wave potential and the potential where emission can first be detected. [c] Half-wave potentials *vs.* sce at a rotating Pt electrode in DMF solution. [d] Peak potential.

values were obtained visually. Several readings by different observers were made for each threshold reported, and the results were found to be reproducible to ±0.05 V. In the instances where the initially generated ion radical showed no detectable stability by cyclic voltammetry, such as the anion of N-methyl-1,3-di-*p*-anisyl-4,7-diphenylisoindole or the cation of 1,3,5,6-tetraphenylisobenzofuran, no emission could be seen when the electrochemical process was reversed regardless of the reverse potential chosen up to and including the background decomposition potential.

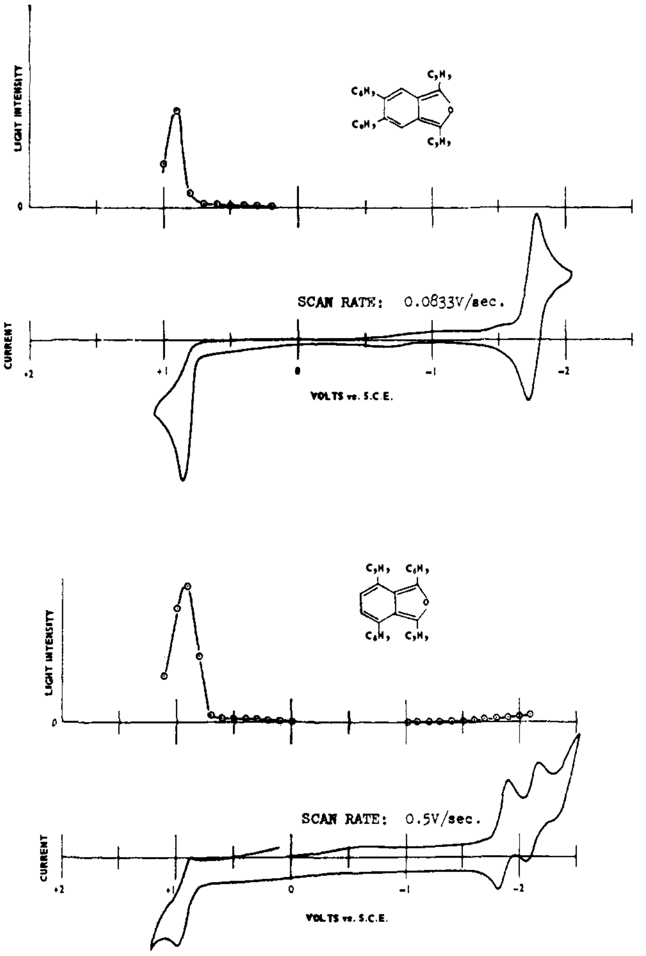

Figure 1. Cyclic voltammograms and potential *vs.* light intensity for two isomeric tetraphenylisobenzofurans in N,N-dimethylformamide.

In a manner similar to the isobenzofurans and isoindoles, the characteristic green fluorescence emission from tetracene could be seen by oxidizing the anion radical of the latter at a platinum electrode which was only +0.45 to +0.49 V *vs.* sce. The tetracene cation is very unstable, and no emission was detected either on its generation or after switching to a more negative electrode potential. In order to ensure that the emission seen on electrochemical treatment of tetracene is not due to generation and electrochemiluminescence from the ubiquitous tetracene-5,12-quinone,[6] the latter was prepared[7] and, as shown in Table I, was found not to be electrochemiluminescent.

Determination of Relative Energy Levels through Spectroscopy. Regardless of whether the oxidations and reductions take place at the electrodes, or in bulk solution, if preannihilative electrochemiluminescence arises through oxidation of anions or reduction of cations to *directly* generate the corresponding neutral molecule in an excited state (*cf.* Discussion), some sort of energy-adding process is required to account for the observed frequency of emission. Thus the energy of the ecl emission maximum[8] (identical with its fluorescence) of 1,3,4,7-tetraphenylisobenzofuran is 13 kcal/mole greater (neglecting entropy change) than the increment between its half-wave reduction potential and the oxidative potential at which the emission can first be detected.[9,10] Similar differences exist between the thermodynamic driving force and the emission energy for the other compounds listed in Table I.

One well-documented process by which emitted quanta may have greater energy than the average input involves triplet–triplet annihilation. We therefore tried to determine the triplet-state properties of molecules which are good electrochemiluminescent substances. Particular attempts were made to gain information about the existence and energy of the triplets of the isobenzofurans and isoindoles listed in Table I. Despite these efforts, the triplet energies could not be determined experimentally. No phosphorescence due to these compounds could be found when they were irradiated in degassed 3-methylpentane glass at 77°K.[11] A search for phosphorescence from naphthyl- and anthracenyl-

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[6] E. Clar and M. Zander, *J. Chem. Phys.*, 43, 3422 (1965), and references therein.

[7] I. M. Roitt and W. A. Waters, *J. Chem. Soc.*, 4060 (1949).

[8] For a list of fluorescence and ecl emission maxima of isobenzofurans and isoindoles, *cf.* ref 2.

[9] Hoijtink[10] has pointed out that even the cation–anion annihilation process should have insufficient energy to reach the excited singlet directly and has suggested the possibility of an intervening triplet annihilation process.

[10] G. J. Hoijtink, comments at the Symposium on Chemiluminescence, Durham, N. C., 1965.

[11] Unless precautions are taken to ensure the purity of the *o*-quinoidal compounds, in a thoroughly degassed environment, strong phosphorescence due to the corresponding *o*-diketone is detected.

substituted isobenzofurans was made in the hope that delayed emission characteristic of the polycyclic hydrocarbon portions of the molecules could be detected. This too proved unsuccessful.

Since halogen substituents enhance intersystem crossing without significantly affecting the singlet and triplet energy levels,[12] 1,3,4-triphenyl-7-*p*-chlorophenylisobenzofuran was prepared and its emission properties were examined. As expected, its fluorescence maximum was nearly identical with that of the unhalogenated compound (533 mμ compared with 530 mμ); however, no delayed emission was detected at 77°K. The room-temperature fluorescence efficiency of the monochloro derivative was virtually the same as 1,3,4,7-tetraphenylisobenzofuran ($\Phi = 0.49$ compared with $\Phi = 0.50$) supporting the evidence that intersystem crossing had not been enhanced to a detectable level.

Efforts were also made to detect isobenzofuran and isoindole triplets by esr and by singlet–triplet absorption spectroscopy. Neither of these techniques produced positive results. Attempts to sensitize isobenzofuran phosphorescence with benzophenone irradiated at 254 and 313 mμ were also unsuccessful. In a recent study of the photooxidation of 1,3-diphenylisobenzofuran,[13] its triplet was implicated as a possible intermediate for part of the reaction although no direct evidence for its presence was demonstrated.

Failure to observe isobenzofuran and isoindole triplets by these methods may be due to inefficient intersystem crossing or exceedingly short triplet lifetimes. The former is anticipated for systems of high fluorescence efficiency, while the latter may be caused by multiple phenyl substitution. Several indirect methods are available for detecting and determining the energy of such triplets. These methods depend on the triplets' chemical reactivity and/or their ability to transfer energy.

The isobenzofurans are readily photooxidized. According to Foote,[14] the most probable mechanisms for photooxidations of furans and similar dienes can be expressed by the following equations.

$$\text{Sens} + h\nu \longrightarrow {}^1\text{Sens} \qquad (1)$$

$${}^1\text{Sens} \longrightarrow {}^3\text{Sens} \qquad (2)$$

$${}^3\text{Sens} + {}^3\text{O}_2 \longrightarrow \text{Sens–O–O–} \qquad (3a)$$

$${}^3\text{Sens} + {}^3\text{O}_2 \longrightarrow \text{Sens} + {}^1\text{O}_2 \qquad (3b)$$

$$\text{Sens–O–O–} + \text{A} \longrightarrow \text{AO}_2 + \text{Sens} \qquad (4a)$$

$${}^1\text{O}_2 + \text{A} \longrightarrow \text{AO}_2 \qquad (4b)$$

If no added sensitizer (Sens) is available, the isobenzofuran may behave as its own sensitizer. In such circumstances whether the reaction involves singlet oxygen or triplet oxygen, the isobenzofuran triplet (I_T) should be an intermediate in the over-all photochemical oxidation. Thus, I_T is either necessary in the direct reaction with ${}^3\text{O}_2$ as in eq 3a, or it is needed to convert ${}^3\text{O}_2$ to ${}^1\text{O}_2$ as in eq 3b. Triplet-quenching substances of sufficiently low energy should, therefore, quench the photosensitized autoxidation of 1,3,4,7-tetraphenylisobenzofuran and thus provide an indication of the latter's triplet energy. We have found, however, that the rate of photosensitized oxidation of a 5×10^{-5} *M* solution of this isobenzofuran in benzene is not affected by a 5×10^{-3} *M* concentration of a variety of triplet quenchers having E_T as low as 29 kcal/mole,[15,16] and even a 0.1 *M* solution of *cis*-stilbene ($E_\text{T} = 36$ kcal/mole) did not diminish the rate of this photooxidation. Thus, either the photochemical oxidation of 1,3,4,7-tetraphenylisobenzofuran does not proceed through, or with the assistance of, its triplet state or its triplet energy is less than 29 kcal/mole. Since ${}^1\text{O}_2$ is only 21 kcal/mole above ground state ${}^3\text{O}_2$, the latter alternative must be regarded as a possibility. In such a case though, the triplet cannot be responsible for the 60-kcal/mole ecl emission from the isobenzofuran.

Effects of Additives on Electrochemiluminescence. Although a great many techniques are available for indirectly determining the intermediacy of triplets in photochemical reactions,[16] most of these are inapplicable in electrochemiluminescence studies. This is because electrochemiluminescence involves electrode reactions in solution, because the energy input is not through irradiation, and, most seriously, because varying experimental parameters characteristic of the system affects the electrochemistry as well as the photochemical processes. However, if triplets play a major role in ecl emission, then their susceptibility to quenching should result in a corresponding effect on the emission. To properly function in an ecl experiment, a triplet quencher must be electroinactive under the experimental conditions, *and* it must be chemically unreactive to all the species present in the emitting system. Dienes and polyenes and their alkyl-substituted derivatives may be expected to be useful triplet quenchers under these conditions. Such compounds are relatively difficult to oxidize and reduce, and they have known low triplet energies which have been determined by singlet–triplet absorption.[17,18] Because of their nonrigid structure, they may assume twisted configurations in the triplet state which should aid in their quenching function.[19] Their reactivity toward most of the components of an electrochemiluminescing system under ordinary conditions should be negligible except possibly toward the ion radicals which are generated. Insofar as the polyenes react with the ion radicals, they should decrease the emission.

Two polyenes with exceptionally low triplet energies are 1,3-cyclohexadiene and *trans*-1,3,5-hexatriene. Singlet–triplet absorption studies have placed the triplet energies of these molecules at 53 and 47 kcal/mole, respectively.[17] When the potential at a platinum electrode in a solution 2 m*M* in 1,3,4,7-tetraphenylisobenzofuran, 0.1 *M* in 1,3-cyclohexadiene, and 0.1 *M* in tetra-*n*-butylammonium perchlorate was cycled between +1.0 and −1.9 V (*vs.* sce) at 0.5 cps with a square-wave generator, the characteristic isobenzofuran fluorescence emission could be detected on each half-cycle. When the voltage span was narrowed to encompass the reduction, but not the oxidation of the isobenzofuran, emission was seen only on the oxidative

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[12] *Cf.* J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, p 302.

[13] T. Wilson, *J. Am. Chem. Soc.*, **88**, 2898 (1966).

[14] C. S. Foote and S. Wexler, *ibid.*, **86**, 3881 (1964).

[15] The acceptors employed were tetraphenylallene ($E_\text{T} = 53$ kcal/mole), diphenylacetylene ($E_\text{T} = 49$ kcal/mole), *trans*-stilbene ($E_\text{T} = 42$ kcal/mole), *cis*-stilbene ($E_\text{T} = 36$ kcal/mole), and 1-phenyl-3,4-dihydronaphthalene ($E_\text{T} \leqq 29$ kcal/mole).[16]

[16] E. F. Ullman and W. A. Henderson, Jr., *ibid.*, **89**, 4390 (1967).

[17] D. F. Evans, *J. Chem. Soc.*, 1735 (1960).

[18] R. E. Kellogg and W. T. Simpson, *J. Am. Chem. Soc.*, **87**, 4230 (1965).

[19] A. J. Fry, R. S. H. Lui, and G. S. Hammond, *ibid.*, **88**, 4781 (1966), and previous papers in this series.

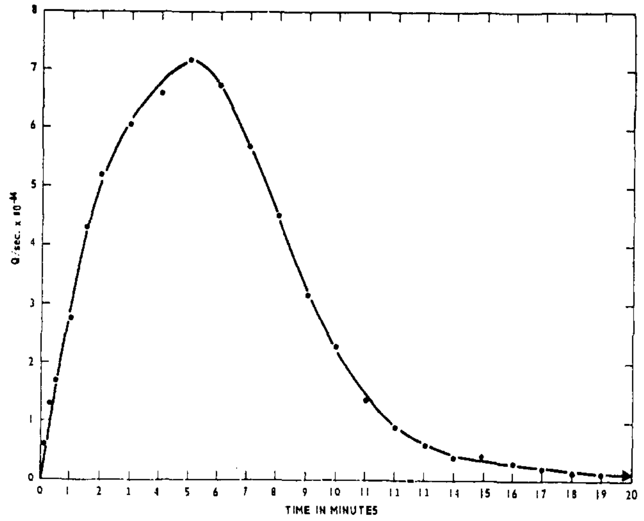

Figure 2. Emission *vs.* time for N-methyl-1,3-di-*p*-anisyl-4,7-diphenylisoindole in DMF solution, 8.0 V applied.

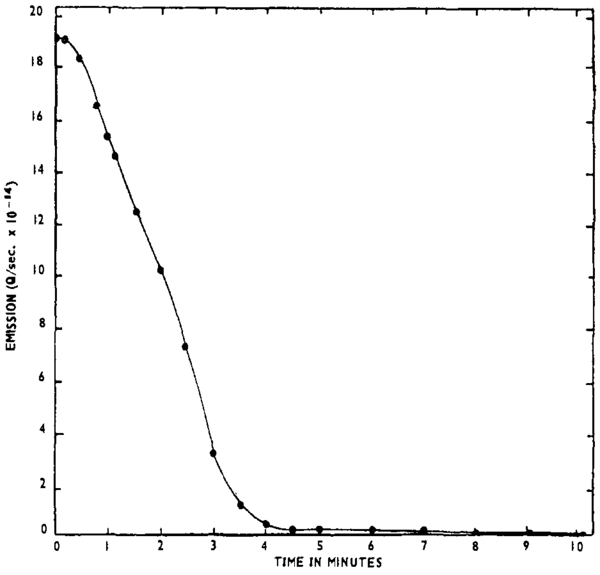

Figure 3. Emission *vs.* time for 1,3,4,7-tetraphenylisobenzofuran in DMF solution, 7.1 V applied.

half-cycle at a threshold of 1.96 V from the half-wave reduction potential. Similarly, if the cation was the only primary species produced, emission was seen only on the reductive half-cycle at a threshold of 1.75 V from the half-wave oxidation potential. As can be seen from Table I, these values are nearly identical with those found in the absence of olefin. In another study 1,3,5-hexatriene was added to an operating ecl cell containing 1,3,4,7-tetraphenylisobenzofuran emitting under preannihilative conditions [emission was seen on cycling at the electrode between -1.90 and $+0.63$ V (*vs.* sce)]. On addition of sufficient 1,3,5-*trans*-hexatriene to make the solution 0.1 *M* in the latter, the emission intensity decreased by 16%. Under the same conditions, however, another similarly emitting system decreased 6% in emission intensity on adding an equivalent amount of *n*-hexane.

Total Quanta Studies. The total number of einsteins emitted as a function of time from an operating ecl cell was measured by means of an integrating sphere and a photomultiplier (*cf.* Experimental Section). Calibration of the cell characteristics and of the sphere and detector were made by employing a dummy cell without platinum electrodes and a chemiluminescent reaction of known quantum efficiency which had an emission spectrum very similar to the ecl emission under investigation. The dummy cell was required because the presence of platinum affects the emission of the chemiluminescent standard.[20]

The results for a typical run employing N-methyl-1,3-di-*p*-anisyl-4,7-diphenylisoindole are shown in Figure 2. The short lifetime of bright emission is due to the large electrode area/solution volume ratio (*cf.* Experimental Section). Another run was carried out, similar to the one shown in Figure 2, which was stopped after 15 min. The loss of fluorescer, as determined by absorption spectroscopy, divided by the quanta emitted during the period indicated a 0.65-einstein/mole loss of fluorescer. As the ϕ_F for this isoindole is 0.5, at least 1.3 excited states were generated per molecule destroyed over the 15-min period. We suspect that this value is substantially higher in the 2–7-min time segment shown in the figure.

The 5-min lag in reaching maximum emission intensity for the isoindole, illustrated in Figure 2, is not generally characteristic of ecl-emitting systems. A more typical emission intensity curve with the cell employed in this study is that of 1,3,4,7-tetraphenylisobenzofuran which is shown in Figure 3. This system produces its maximum emission intensity at the outset and then decays to a very low level within 5 min.

It is, of course, also of interest to learn the current efficiency of ecl emission; however, when one employs 60-cps alternating square-wave voltages across parallel platinum grid electrodes, a large charging current exists as well as the Faradaic current responsible for the luminescence process.[21] This creates two problems. It means that a substantial fraction of the coulombs passed are not in any way involved in the light-producing Faradaic process. In addition, the resultant high *IR* drop occurring at the initial part of the square pulse necessitates the use of a high cell voltage in order to maximize the light intensity, and this in turn raises the possibility that undesirable side reactions will occur at the end of the square-wave pulse where the *IR* drop is a minimum. In order to evaluate the total current (charging + Faradaic) effects on ecl emission for short periods, the emission from the calibrated cell was measured in the integrating sphere while the current passed in either direction was measured across a 10.00-ohm resistor placed in series with the cell. The current was measured with a Dymec voltage-to-frequency converter and two General Radio Co. Digital frequency counters. The transistorized switch was adjusted so that the currents passed in both directions were essentially equal (< 1% deviation after 5 min).

The results of one such study, employing N-methyl-1,3-di-*p*-anisyl-4,7-diphenylisoindole as the emitter, are illustrated in Figure 4. The coulombs passed and quanta emitted were *summed* every 30 sec, and these sums were plotted *vs.* elapsed time for the first 10 min of the run.

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(20) Platinum catalyses the decompositions of hydrogen peroxide which is one of the components of the chemiluminescence standard (*cf.* Experimental Section).

(21) For a discussion of this problem, *cf.* E. R. Brown, T. G. McCord, D. E. Smith, and D. D. DeFord, *Anal. Chem.*, **38**, 1119 (1966).

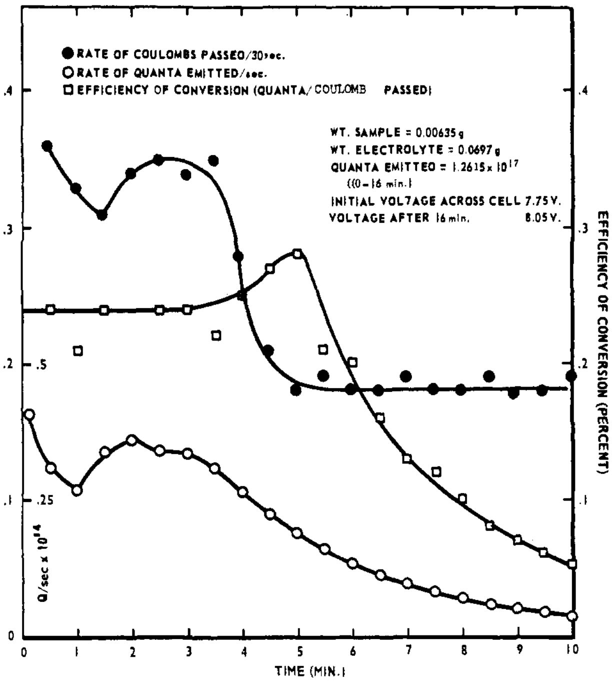

Figure 4. Current–emission study of N-methyl-1,3-*p*-anisyl-4,7-diphenylisoindole.

Also plotted in the figure is the efficiency of emission for each 30-sec increment, obtained by dividing the quanta produced by the coulombs passed in each time segment. This gives the over-all coulombic efficiency of the cell, but not the efficiency relative to the Faradaic process alone which *must* be greater.

The rate of current flow is seen to follow the rate of light emission through an initial minimum in electrochemiluminescence rate and then drop sharply for a second time, this time paralleling the permanent decay of the light emission rate. After about 5 min, when the light emission has clearly started into a sharp decline, the energy conversion is at its highest level since the current has gone into a *relatively sharper* decline. Soon after this, the current levels off, and this combined with the continued decrease in emission results in a steady decline in energy conversion efficiency. At the maximum, at about 5 min, there is about a 0.3% efficiency of electrical energy conversion to light. Since the fluorescer has a 50% fluorescence efficiency,[2] there must be a 0.6% over-all coulombic efficiency in creation of excited states.

Discussion

The detailed studies of Parker[22] have indicated that triplet–triplet annihilation of tetracene in solution is energetically incapable of producing the tetracene-excited singlet. The observation of preannihilative fluorescence emission through oxidation of the stable tetracene anion radical, despite a thermodynamic driving force insufficiency of 13 kcal/mole, indicates that an energy adding process other than triplet–triplet annihilation may be operative in this system. Although no direct measurements of the lowest triplets of the isobenzofurans or isoindoles was possible, there are several assumptions that can be made as to their properties suggesting that triplet–triplet annihilation is not significantly involved in their ecl emission. The isobenzofuran π-electron system is isoelectronic with naphthalene (E_T = 60.8 kcal/mole),[23] and, as phenyl substituents do not significantly lower the triplet energy of the latter,[24] there is little reason to expect that the ($\pi \rightarrow \pi^*$) triplet of the isobenzofuran is exceptionally low. A less likely possibility is that a nonbonding electron pair, available on the ether oxygen, results in the lowest triplet of the isobenzofurans (but not the isoindoles) being $n \rightarrow \pi^*$. There is usually a very small separation between $^3(n \rightarrow \pi^*)$ and $^1(n \rightarrow \pi^*)$ transitions,[25] and the $^1(n \rightarrow \pi^*)$ of the isobenzofurans could not be found with absorption at longer wavelength than the strong $\pi \rightarrow \pi^*$ band with a maximum at 410 mμ (70 kcal/mole). The $^3(n \rightarrow \pi^*)$ is, therefore, also of greater energy than 47 kcal/mole relative to the ground state and should be susceptible to quenching by *trans*-1,3,5-hexatriene and other polyolefins. A study of the phosphorescence emission from several phenyl-substituted naphthalenes[24] has indicated that multiple substitution drastically shortens triplet lifetime. 1,4,5,8-Tetraphenylnaphthalene, like 1,3,4,7-tetraphenylisobenzofuran, does not phosphoresce at 77°K, although the former has a relatively low fluorescence efficiency (0.29 at 22° in DMF). The fact that compounds with short triplet lifetimes are among the brightest ecl emitters mitigates against triplets playing an important role in their electrochemical emission processes.

The evidence points to at least the major portion of isobenzofuran and isoindole electrochemiluminescence proceeding without the intermediacy of triplets. The finding that oxidation of the phenanthrene anion, however, does produce the phenanthrene triplet,[26] detectable both through the emission of phosphorescence and the susceptibility of the phosphorescence emission to triplet quenching, shows that different molecules may be brought to excited states of different multiplicity by electrochemical means and that broad generalities about the mechanism of electrochemiluminescence cannot be made.

While the source of emission must be a molecule in an electronically excited state, that molecule need not be directly formed, or even be involved, in the processes which result in the liberation of the energy required for the excitation. Rauhut, Roberts, and Semsel[27] have recently illustrated this in their chemiluminescence studies. They found that the reaction of oxalic acid derivatives with hydrogen peroxide results in the liberation of energy in a form which is capable of being transferred to a nonreacting fluorescent molecule which is also present, thus raising the latter to its excited, emitting state. This type of energy transfer may be postulated to occur in electrochemical reactions when a species is produced which undergoes unimolecular decomposition or reacts with its environment.

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[22] C. A. Parker, *Advan. Photochem.*, **2**, 370 (1964).

[23] Reference 12, p 297.

[24] The phosphorescence emission onset of 1-phenylnaphthalene is close to that of naphthalene at 77°K (478 mμ, compared to 465 mμ), but its lifetime is halved: unpublished observation of J. B. Gallivan.

[25] S. P. McGlynn, F. J. Smith, and G. Cilento, *Photochem. Photobiol.*, **3**, 269 (1964).

[26] A. Zweig, D. L. Maricle, J. S. Brinen, and A. H. Maurer, *J. Am. Chem. Soc.*, **89**, 473 (1967); D. L. Maricle, A. Zweig, A. H. Maurer, and J. S. Brinen, *Electrochem. Acta*, in press. Evidence has been obtained for triplet intermediates in other instances also: A. Weller and K. Zachariasse, *J. Chem. Phys.*, **46**, 4984 (1967).

[27] M. M. Rauhut, B. G. Roberts, and A. M. Semsel, *J. Am. Chem. Soc.*, **88**, 3604 (1966); see A. N. Fletcher and C. A. Heller, *J. Phys. Chem.*, **71**, 1507 (1967), for a further pertinent illustration.

An example of such a phenomenon may be the rubrene fluorescence emission which occurs on electrochemical generation of the unstable cation radical of rubrene in dimethylformamide solution.[4] It appears that this cation radical undergoes a reaction with solvent, and possibly oxygen.[28] The energy of the reaction may then be transferred to unoxidized rubrene, raising the latter to an excited state. A possibly related finding[29] is that the carbanion R^- related to Koelsch's radical $R\cdot$ reacts with oxygen in a wide variety of aprotic solvents with the partial stoichiometry $2R^- + O_2 \rightarrow R\cdot +$ other products, in which the first step appears to be a one-electron transfer from the carbanion to an oxygen molecule: $R^- + O_2 \rightarrow R\cdot + O_2\cdot^-$.

Table II shows four mechanisms which may possibly account for the energy-adding phenomenon associated with preannihilative ecl emission on oxidation of anions. Four similar processes can be postulated for the preannihilative emission associated with reduction of cations. Due to the results of the findings with tetracene, the first of these processes, triplet–triplet annihilation, cannot be regarded as generally applicable.

Table II. Some Possible Mechanics for Preannihilative Ecl Associated with Oxidation of Anion

1. Triplet–Triplet Annihilation

$$R\cdot^- + [\mathrm{Ox.}] \longrightarrow R^T$$
$$2R^T \longrightarrow R^{S_1}$$
$$R^{S_1} \longrightarrow R^{S_0} + h\nu$$

2. Impurity Scheme I

$$R + [\mathrm{Red.}] \longrightarrow R\cdot^- + \mathrm{Imp.}$$
$$\mathrm{Imp.} + [\mathrm{Ox.}] \longrightarrow \mathrm{Imp.}^+$$
$$\mathrm{Imp.}^+ + R \longrightarrow R^{S_1} + X$$
$$R^{S_1} \longrightarrow R^{S_0} + h\nu$$

3. Impurity Scheme II

$$\mathrm{Imp.} + [\mathrm{Ox.}] \longrightarrow \mathrm{Imp.}^+$$
$$\mathrm{Imp.}^+ \longrightarrow \mathrm{Imp.\ D}$$
$$\mathrm{Imp.\ D} + R\cdot^- \longrightarrow R^{S_1} + \mathrm{Imp.\ D}^-$$
$$R^{S_1} \longrightarrow R^{S_0} + h\nu$$

4. Aggregate Scheme

$$(R\cdot^-)_x + x[\mathrm{Ox.}] \longrightarrow R^{S_1} + (x-1)R^{S_0}$$
$$R^{S_1} \longrightarrow R^{S_0} + h\nu$$

It has been suggested[3] that impurities play a role in the preannihilative emission phenomenon. Since it has been shown that the quantum yield of annihilative emission is only of the order of 1% and since the preannihilative emission intensity is approximately two orders of magnitude less intense than the annihilative intensity, it would take a *ca.* 10^{-7} *M* concentration of impurity to be completely responsible for the emission. Such impurity may arise on the first step of the double-potential-step experiment. This step, involving initial production of the ion radical, *is required* for emission to be seen on the second step. Two general schemes for impurities functioning in the preannihilative emission can be envisaged. In the first scheme the impurity is generated in the initial step, along with the anion radical, and then on oxidation it decomposes exothermally with energy transferred to the fluorescer. This scheme does not require fluorescer anion-radical stability. For this reason it can be excluded, since, if it were operative, there would be no reason why preannihilative emission is not detected, for example, on the oxidation cycle after reduction of N-methyl-1,3,-di-*p*-anisyl-4,7-diphenylisoindole (*cf.* Table I) to an unstable species.

Another impurity scheme (II) would have (for the oxidation-of-anion process) the impurity undergo electrochemical oxidation followed by a fast chemical reaction at the threshold potential to generate a *stronger* oxidant, an impurity decomposition product (Imp. D), which then oxidized the anion radical with sufficient energy to produce the excited singlet without thermodynamic misgivings. If the impurity were present before the electrochemical process began, one would be able to reverse the double-potential-step experiments (that is, first generate the oxidant and then the anion) and get light emission. When this was tried, however, no emission was seen. If the oxidant is not stable, one may expect to remove it by electrolysis. Such a procedure did in fact remove some but *not all* of the preannihilative emission from rubrene-containing systems,[3] showing that in this case the impurity scheme may indeed be operative. If the impurity is generated by unimolecular decomposition of the ion radical, such pretreatment would, of course, be of no avail. One impurity which may be anticipated under the experimental conditions is the protonated anion radical, $RH\cdot$. This species could possibly supply the energy on oxidative decomposition. However, when the corresponding reduction of cation radicals preannihilative emission process is considered, one must postulate that the comparable product, RX, resulting from electrophilic attack of the cation radical on some component of the system, produced together with the cation radical R^-, undergoes reduction to RX^-. Such a species would be even less likely to react with solvent than RH^+. Even if it did decompose, it would not be expected to do so to form a stronger reductant (necessary to oxidize the cation radical with sufficient energy to reach the excited singlet state directly). Virtually all spontaneous chemiluminescence processes involve oxidation,[30] and the observation of preannihilative emission in electrochemical reductive processes is not compatible with a mechanism involving spontaneous decomposition of impurities. A further observation which is difficult to reconcile with either impurity mechanism is that the increments of potential needed to reach the threshold of detectable emission are usually very similar for both the oxidative and reductive processes for the same molecule. This requires that the same potential increment be subtracted from the anodic and cathodic half-wave potentials in order to produce both the oxidant and reductant. As such fortuitous occurrences seem highly unlikely, this mechanism must be regarded as unreasonable.

In a preliminary communication[1] it was suggested that ion-radical aggregates may be the species oxidized or reduced at the electrodes under preannihilative conditions, and that multiple electron transfer to (or from) the aggregate may be accomplished with an accumulation of the excess energy on one of the resulting neutral molecules. Such a mechanism would seem to adequately account for all the experimental evidence so far available.

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(28) D. L. Maricle and A. H. Maurer, unpublished observations.

(29) J. G. Pacifici, J. F. Garst, and E. G. Janzen, *J. Am. Chem. Soc.*, 87, 3014 (1965).

(30) F. McCapra, *Quart. Rev.* (London), 485 (1966).

Such aggregate species are not favored by low ion-radical concentrations, polar solvents such as DMF, or counterions such as quaternary ammonium salts or perchlorate. However, conditions near the electrode may permit their formation, and only small concentrations are needed to achieve the low luminescence levels which are observed. A similar overpotential requirement for emission from both oxidation of anion and reduction of cation aggregates may reasonably be anticipated, and the influence of impurities, even by their incorporation into the aggregate, may also be expected.

Much evidence has continued to accumulate that ion radicals, even in dilute solution, are capable of exchanging energy. Miller and Adams[31] found that the spin–spin exchange rates of a wide variety of organic radicals and radical ions are purely diffusionally controlled in the 5×10^{-4} to 5×10^{-3} *M* range and noted there must be a considerable overlap of the wave functions of the unpaired electrons for this to take place. Hirota[32] found that in various ether solutions of aromatic ketyls of concentration as low as 10^{-3} *M*, the *predominant* species are contact ion quadruplets where a pair of solvated cations are shared by two anion radicals.

As these and other investigators[33–36] have recently shown, one may adduce evidence for ion aggregate species by a variety of methods. Relating the presence of such aggregates to the preannihilation process with certainty will require further effort. Since aggregate cation radicals are as likely as aggregate anion radicals, this mechanism affords a more plausible and consistent explanation of the preannihilative emission than an uncritical dismissal as due to "impurities."

Experimental Section

Compounds. All materials employed in this investigation, except 1,3,4-triphenyl-7-*p*-chlorophenylisobenzofuran, have been described previously.[1–3,7] 1,3,5-*trans*-Hexatriene was obtained in sealed vials from the Aldrich Chemical Co. and was used without purification immediately after opening the vial. 1,3-Cyclohexadiene was obtained from the same source and was distilled before use.

1-Phenyl-4-*p*-chlorophenyl-1,3-butadiene. Cinnamyltriphenylphosphonium bromide[37] (27.0 g, 0.06 mole) was mixed with 10.5 g (0.75 mole) of *p*-chlorobenzaldehyde (Eastman Kodak Co.) in 250 ml of ethanol. A solution of 0.7 g (0.1 g-atom) of lithium in 100 ml of ethanol was added, and the combined material was refluxed for 2 hr, then concentrated *in vacuo* to *ca.* 100 ml. The resulting material was filtered and the tan solid was recrystallized from ethanol to yield 8.1 g (56%) of tan plates, mp 161–162°, lit.[38] 161°.

3-Phenyl-4,5-dibenzoyl-6-*p*-chlorophenylcyclohexene. A mixture of 8.1 g (0.034 mole) of 1-phenyl-4-*p*-chlorophenyl-1,3-butadiene and 8.1 g (0.033 mole) of 1,2-dibenzoylethylene (Eastman Kodak Co.) in 50 ml of 1-butanol was refluxed for 4 hr. On cooling, a pale yellow precipitate was formed. This material on recrystallization from ethanol gave first a pale yellow product, mp 158–160°, which was not further investigated, and on further concentration, 5.3 g (33%) of a sharp melting compound, mp 180–181°.

Anal. Calcd for $C_{32}H_{25}ClO_2$: C, 80.57; H, 5.28. Found: C, 80.77; H, 5.08.

1-Phenyl-2,3-dibenzoyl-4-*p*-chlorophenylbenzene. A refluxing solution of 5.95 g (0.0125 mole) of 3-phenyl-4,5-dibenzoyl-6-*p*-chlorophenylcyclohexene was treated dropwise with a solution of 4.0 g (0.025 mole) of bromine in 50 ml of chloroform over 20 min. The mixture was refluxed for 10 min further, and then the solvent was evaporated under nitrogen to give a yellow oil. Trituration of the oil with 25 ml of methanol gave a white solid. Recrystallization, first from benzene–heptane, then from ethanol, gave 2.65 g of the crude desired product, mp 162–165°, which was used in the subsequent reaction without further purification.

1,3,4-Triphenyl-7-*p*-chlorophenylisobenzofuran. A solution of 2.65 g (*ca.* 5.6×10^{-3} mole) of the above 1-phenyl-2,3-dibenzoyl-4-*p*-chlorophenylbenzene and 3.0 g (0.075 mole) of sodium hydroxide in 75 ml of ethanol was brought to reflux. To the refluxing solution was added 3.0 g (0.046 g-atom) of pretreated zinc dust. After 4 hr of refluxing, the solution was filtered, while hot, into 75 ml of glacial acetic acid. The yellow precipitate was sublimed and resublimed. The resublimed material, 1.1 g, had mp 254°.

Anal. Calcd for $C_{32}H_{21}ClO$: C, 84.11; H, 4.63. Found: C, 83.86; H, 4.77.

The uv spectrum showed λ_{max} 405 mμ (ε 14,800) and 327 mμ (ε 5830) in N,N-dimethylformamide; a fluorescence maximum at 533 mμ (cor), $\Phi = 0.49$, in N,N-dimethylformamide was present.

Electrochemical Techniques. The double-potential-step experiments were run at a 0.25-in. length of 0.04-in. diameter platinum wire electrode immersed in a 10^{-3} *M* solution of the fluorescer in DMF, with 0.1 *M* tetrabutylammonium perchlorate as the supporting electrolyte, in a three-electrode polarographic cell. The platinum electrode was placed within 1 mm of a fine glass frit connected to the reference compartment of the cell.[26] The reference compartment contained an additional 5 ml of the emitting solution being tested and was connected by a salt bridge (0.5 *M* tetra-*n*-butylammonium perchlorate in DMF) to a saturated calomel reference electrode. A polyvinyl alcohol film separated the test solution in the reference compartment of the polarographic cell from the salt bridge.[26] The operating cell was purged with dry oxygen-free nitrogen.

A three-electrode operational-amplifier-based electronic polarograph was used to record the cyclic voltammograms. The double-potential-step wave form was derived by driving a relay with the square-wave output of a Hewlett–Packard 202A signal generator. This relay applied and removed an adjustable voltage (battery and variable resistor) from the input of the polarograph at a precisely controlled rate. Synchronization with the free-running signal generator was accomplished by manual switching.

The light was detected with an Aminco photomultiplier microphotometer equipped with a 1P21 photomultiplier. In order to avoid the relatively long time constant of the Aminco amplifier, the input probe of a 502A Tektronix dual-beam oscilloscope was connected directly to the current-measuring resistor, thereby by-passing the Aminco amplifier and substituting the oscilloscope amplifier. A Polaroid camera was used to record current and light pulses simultaneously.

A 5×10^{-4} *M* solution of 1,3,4-triphenyl-7-*p*-chlorophenylisobenzofuran in methyltetrahydrofuran was prepared under subdued light and immediately transferred to a vacuum line where it was carefully degassed. Excitation of the sample with 365-mμ light resulted in no detectable delayed emission in the 350–750-mμ region at 77°K.

Effects of Triplet Quenchers on Photooxidation of 1,3,4,7-Tetraphenylisobenzofuran. A stock solution containing a 5×10^{-5} *M* concentration of the isobenzofuran in benzene was poured into several quartz spectrophotometer cells and to these was added enough of the various triplet quenchers to make the solutions 0.005 to 0.1 *M* in the latter. Together with a control containing no added quencher, the solutions open to the atmosphere were irradiated simultaneously for 15–25 min with a Hanovia high-pressure lamp using Corning filters No. 7380 and 5860 to absorb all light below 365 mμ.

The rate of decomposition, as determined by the decrease in the 1,3,4,7-tetraphenylisobenzofuran absorption band at 410 mμ, was found to be unaffected by the added substances. Only triphenylethylene (E_T = 40 kcal/mole) showed the apparent ability to slow the rate of photodecomposition, and this was found to be due to the fact that this compound absorbs appreciably at >365 mμ, and thus diminishes the radiation received by the tetraphenylbenzofuran.

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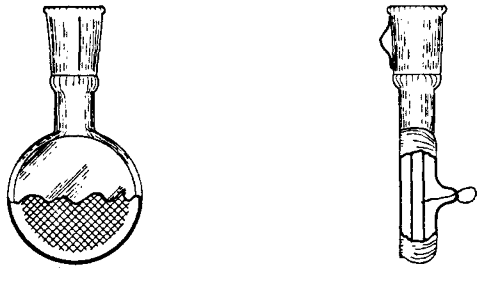

Figure 5. Electrochemiluminescence cell employed in the integrating-sphere studies.

Quantum-Yield Measurements. A 10-in. sphere was coated on the inner side with barium sulfate sphere paint[39] to give a surface with reflectance of 95% or better from 400 to 700 mμ.[40,41] A 1-in. diameter hole and a 1.5-in. diameter hole were cut into the sphere so as to be on the same great circle, having an arc of 180° between centers. A 1P28 photomultiplier detector was mounted on a holder having a 1-in. diameter tubulation extending 0.6 cm into the sphere. A ground-glass plate was attached to the end of the tube which extended into the sphere, and provision was made for inserting metallic screens into the tube to control the light level observed by the detector. The readout unit and power supply for the photomultiplier was an Aminco No. 10-213 microphotometer. The 1.5-in. diameter opening of the sphere was positioned on top so that the ecl cell (*cf.* Figure 5) could be suspended vertically into the center of the sphere. The platinum grid electrodes of the ecl cell were 80 mesh, 2.5 cm in diameter, and spaced 1 mm apart. The electrical leads acted as a suspension with terminals ending at a cap resting in the sphere opening. The sphere thus assembled was light tight, and essentially all of the light emitted impinged on the sphere wall, to be integrated, before measurement.

In order to calibrate the intensity of the emission recorded with the photomultiplier in terms of einsteins emitted, the cell shown in Figure 5 less its platinum electrodes was filled with a chemiluminescent solution,[27] containing N-butyl-4-butylaminonaphthalimide (Calofluor Yellow 7G$^{\mathrm{R}}$) as the emitting species and placed in the integrating sphere. Simultaneously, this solution was poured into a cell of a chemiluminescence apparatus[27] in which the quanta per second emitted by the sample could be measured. The values obtained were correlated with the light-intensity measurements obtained on the photomultiplier attached to the integrating sphere to obtain a constant, *k*, by which the photomultiplier reading would be converted to quanta per second. In instances where the spectral distribution of the ecl emission differed significantly from the chemiluminescence standard, *k* was changed to reflect the known spectral response curve of the photomultiplier tube. A small lamp (grain of wheat) operated at known low voltage was inserted into the sphere periodically to check the constancy of the readout of the sphere assembly.

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(39) Reflectance grade barium sulfate (Bausch & Lomb) with an acrylic latex binder was employed.

(40) Measured by comparison with a National Bureau of Standards reflectance standard.

(41) The use of reflectance spheres is described in "Absolute Calibration of Reflectance Standards," ASTM Designation E306,1966.

The Photolysis of 1,1'-Azoisobutane Vapor at 3660 A. The Reactions of the Isobutyl Free Radical[1]

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Abstract: The vapor-phase photolysis of 1,1'-azoisobutane was studied in experiments at wavelength 3660 A and at various temperatures and pressures. The product rate data fit well the suggested reaction scheme involving an excited azoisobutane molecule and reactions of the isobutyl free radical. The ratio of rate constants for the disproportionation and combination reactions of the isobutyl radical was estimated to be 0.075 ± 0.007 (25–168°). Rate constants for the H-atom abstraction and the decomposition reactions of the isobutyl radical were derived assuming the rate of the isobutyl combination reaction to be 2.2×10^{13} cc/mole sec: $i\text{-C}_4\text{H}_9 + (i\text{-C}_4\text{H}_9)_2\text{N}_2 \rightarrow i\text{-C}_4\text{H}_{10} + \text{C}_4\text{H}_8\text{N}_2\text{C}_4\text{H}_9$ (3), $k_3 \cong 3.2 \times 10^{10}e^{-6.7/RT}$ cc/mole sec; $i\text{-C}_4\text{H}_9 \rightarrow \text{C}_3\text{H}_6 + \text{CH}_3$ (5), $k_5 \cong 2.4 \times 10^{12}e^{-31 \pm 2/RT}$ sec^{-1}. These rate data were used with published data for the *sec*-butyl decomposition reaction, enthalpy and entropy data, to predict the kinetic reason for the dominance of reaction 10 over 9 [$\text{CH}_3 + \text{C}_3\text{H}_6 \rightarrow$ *sec*-C_4H_9 (10), $\text{CH}_3 + \text{C}_3\text{H}_6 \rightarrow i\text{-C}_4\text{H}_9$ (9)]; the data suggest that it is largely the result of an *A*-factor difference between the two reactions. From the effects of pressure and temperature on the quantum yield of nitrogen, an estimate was obtained for the rate constant for the excited azo molecule decomposition reaction: $(i\text{-C}_4\text{H}_9)_2\text{N}_2{}^* \rightarrow 2i\text{-C}_4\text{H}_9 + \text{N}_2$ (B), $k_\text{B} \leq 4.5 \times 10^9e^{-4.8/RT}$ sec^{-1}. If the excited singlet were the reactant in B, then fluorescence emission should be observable from the azoisobutane. No emission was detectable even in experiments at −180°.

There is now very little quantitative information available on the reactions of the isobutyl free radical, although its unique structure makes its kinetic characterization of special interest. Since it has but one H atom per radical which by abstraction leads to olefin, one expects this radical to have an unusually low rate constant for the disproportionation reaction. Indeed Kraus and Calvert[2] estimated that the ratio of the rate constants for the disproportionation and combination

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(1) (a) Presented at the Robert Livingston Photochemical Symposium, Minneapolis, Minn., May 9, 1967; (b) Division of Physical Chemistry, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, paper 44.

(2) J. W. Kraus and J. G. Calvert, *J. Am. Chem. Soc.*, **79**, 5291 (1957).