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## Excimer Formation and Emission *via* the Annihilation of Electrogenerated Aromatic Hydrocarbon Radical Cations and Anions

*Sir:*

The formation of singlet excited hydrocarbon molecules (R*) *via* the reaction of aromatic hydrocarbon radical cations (R+) with the corresponding radical anions (R−) has been reported.[1] The results obtained from a detailed study of 9,10-diphenylanthracene and qualitative studies of other hydrocarbons led to the inference of the generality of this reaction which is related to the chemiluminescent oxidations of various radical anions.[2] *A priori*, two related pathways can be envisioned for the R+–R− reaction.

$$R^+ + R^- \longrightarrow R + R^* \text{ (singlet and/or triplet)} \quad (1)$$
$$R^+ + R^- \longrightarrow (R_2)^* \quad (2)$$
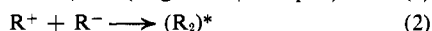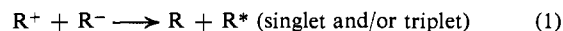
We have studied the course of this reaction for several flat aromatic hydrocarbons unencumbered by bulky substituents and found that path 2, leading to the formation of an excimer,[3] is a common process. These observations have interesting mechanistic implications and we have been able to demonstrate the existence of some previously unknown excimers. Our results and known fluorescent properties of these hydrocarbons are summarized in Table I.



Figure 1. Fluorescence (———) and electroluminescence (– – – –) spectra; perylene crystalline excimer (–·–·) shown in 1a.

red from the normal fluorescence of the same solution. This is a characteristic feature of excimer fluorescence and is a compelling reason for the choice of path 2 for the mechanism of the reaction. The only unsubstituted hydrocarbon which failed to yield excimer emission was naphthacene. It has never been observed to form an excimer and this may be a consequence of its marked tendency to undergo self-quenching.

**Table I**[a]

| | Excimer | | Self- | Triplet | Annihilation | Electroluminescence | |
| | Soln. | Exptl. | quenching | monomer | Excimer | Monomer | Excimer |
|---|---|---|---|---|---|---|---|
| Anthracene | − | − | + | + | − | + | + |
| 9,10-Dimethylanthracene | − | − | − | 0 | 0 | + | + |
| 9,10-Diphenylanthracene | − | − | − | − | − | + | − |
| Phenanthrene | − | − | + | + | − | + | + |
| Pyrene | + | + | + | + | + | 0 | 0 |
| Naphthacene | − | − | + | − | − | + | − |
| Rubrene | − | − | − | 0 | 0 | + | − |
| Perylene | + | + | + | + | − | − | + |
| 3,4-Benzpyrene | + | + | + | + | + | − | + |

[a] Symbols: + indicates that it has been observed; − that it has been found not to be present; and 0 that no results are available.

The chemiluminescent reaction of R+ and R− was achieved by alternating-current electrolysis of a solution of the hydrocarbon in acetonitrile or dimethylformamide.[1,4] The emission spectra commonly contained a broad structureless band shifted toward the

(1) R. E. Visco and E. A. Chandross, *J. Am. Chem. Soc.*, **86**, 5350 (1964); see also D. M. Hercules, *Science*, **145**, 808 (1964), and K. S. V. Santhanam and A. J. Bard, *J. Am. Chem. Soc.*, **87**, 139 (1965).
(2) E. A. Chandross and F. I. Sonntag, *ibid.*, **86**, 3179 (1964).
(3) T. Forster and K. Kasper, *Z. Elektrochem.*, **59**, 977 (1955).
(4) The chemiluminescence, which is modulated at the same or twice the frequency (15–400 c.p.s.) of the voltage imposed on the cell, was measured by modulation spectrometry[5] which employed phase sensitive detection synchronized to the input frequency. The spectra were easily reproducible.
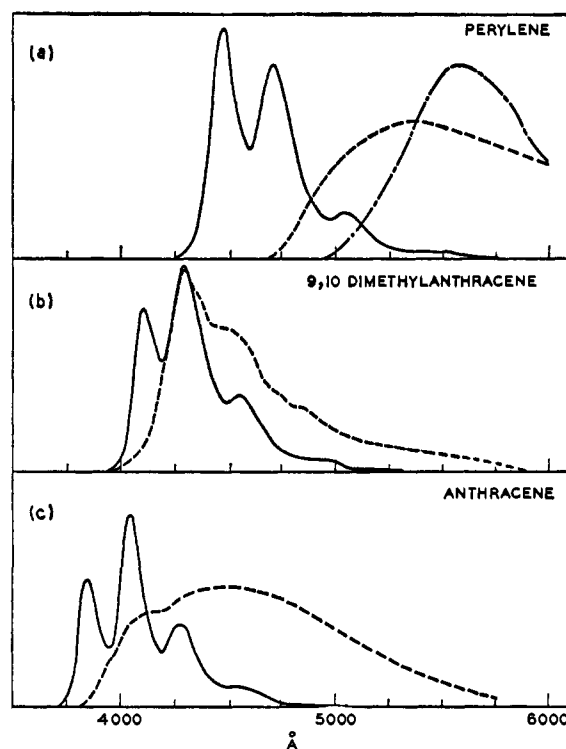(5) R. M. Hexter, *J. Opt. Soc. Am.*, **53**, 703 (1963); H. Labhart, *Helv. Chim. Acta*, 47, 2279 (1964).

The chemiluminescence and normal fluorescence spectra of these solutions (0.001–0.01 *M*) are presented in Figure 1 which also includes the known crystalline state excimer emission of perylene.[6]

The emission from perylene (Figure 1a) resembles that of the known excimer and contrasts sharply with the fluorescence of the same solution which has no excimer component. Other hydrocarbons exhibit both monomer and excimer fluorescence. 9,10-Dimethylanthracene, 9,10-diphenylanthracene, and rubrene were electrolyzed under potentiostatic conditions which restricted the electrode potential to the range between the first oxidative and reductive potentials of the hy-

(6) B. Stevens, *Spectrochim. Acta*, 18, 439 (1962).

drocarbon.[7] This ensures that the $R^+$–$R^-$ reaction is the predominant one. The other hydrocarbons were electrolyzed at constant applied voltage. The emission from the 9,10-dimethylanthracene solution (Figure 1b), attributable to the $R^+$–$R^-$ reaction, clearly has a broad component to the red of the fluorescence.[8] Anthracene (Figure 1c) yields mainly excimer emission. The difference between the latter two compounds is in accord with the expected destabilization of the excimer by the methyl groups, a steric effect which is of critical importance in 9,10-diphenylanthracene and rubrene[9]; these two hydrocarbons give rise only to normal monomer fluorescence under all conditions. The absence of any chemiluminescence other than monomer fluorescence in these cases as well as in naphthacene is evidence against the intervention of an unknown reaction which might be responsible for the diffuse long wave length bands. Phenanthrene yields comparable amounts of monomer and excimer, while 3,4-benzpyrene gives only excimer fluorescence.

The presence of a broad structureless emission band which we have interpreted as excimer fluorescence is explicable only on the basis of the $R^+$–$R^-$ reaction. This implies strongly that the mechanism requires the close approach of $R^+$ and $R^-$ before electron transfer can take place and suggests that electron tunneling across appreciable distances is not a likely event.

The structure of an excimer and the possibility of isomeric excimers which may be separated by energy barriers is a point that we wish to consider in view of the data obtained from anthracene. Anthracene and phenanthrene are well known to undergo self-quenching via the interaction of $^1R^*$ with R, whereas 9,10-diphenylanthracene and rubrene fail to do so because of steric hindrance. The excimer of anthracene thus formed can revert to its components or undergo non-radiative decay to ground-state molecules.[10] Triplet polyacenes undergo annihilation by both a collision process and by long-range interaction.[11–13] The latter leads only to normal fluorescence. The collision process, in the case of benzpyrene and pyrene, is the only explanation for the presence of delayed excimer fluorescence. There is evidence available to support the formation of at least one nonradiative excimer of anthracene, but there is no report of any excimer emission from anthracene. We have concluded that excimer emission predominates in $R^+$–$R^-$ annihilation, and we must conclude further that another excimer of anthracene (formed from $R^+$ and $R^-$) exists and that in contrast to those (or the one) formed from $^1R^*$ + R or $^3R^*$ + $^3R^*$ it is capable of direct fluorescent emission. The simplest explanation is that the formation of the excimer as a charge-transfer state can yield a different excimer. It is puzzling that the collision of two triplets which eventually yields $^1R^*$ does not yield some of this radiating excimer, for there is generally sufficient energy available (3.5 e.v. for anthracene). Apparently

(7) We have observed the e.s.r. spectrum of the radical cation.
(8) Short wave length emission is decreased by reabsorption of the fluorescence at the relatively high (0.01 M) concentration used.
(9) E. J. Bowen, Trans. Faraday Soc., 50, 100 (1954).
(10) The formation of dianthracene is a minor process: A. Dammers de Klerk, Mol. Phys., 1, 141 (1958).
(11) G. Porter and P. West, Proc. Roy. Soc. (London), A279, 302 (1964).
(12) C. Tanaka, J. Tanaka, E. Hutton, and B. Stevens, Nature, 198, 1192 (1963).
(13) C. A. Parker, ibid., 200, 331 (1963).

the charge-transfer state is of considerable importance for emission and may require an appreciable activation energy for its formation. These same arguments are applicable to 9,10-dimethylanthracene and to phenanthrene.

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## Direct Infrared Determination of the Resonance Interaction in Monosubstituted Benzenes

Sir:

An important consideration in aromatic chemistry is the amount of electronic interaction between various substituents and the nucleus. The usual method of estimation involves the measurement of reaction rates, position of equilibria, or physical constants of a series of disubstituted benzenes containing one fixed substituent chosen for this purpose. Unfortunately, the fixed substituent employed as a probe may itself affect the required interaction between the other substituent and the ring. Nevertheless, measurements can be made in cases where such further perturbation is restricted and the results are usually expressed as $\sigma^0$ values.[1] The interaction can be considered to be made up of inductive and resonance contributions as shown in the equation $\sigma^0 = \sigma_I + \sigma_R{}^0$, where $\sigma_I$ represents the inductive effect and $\sigma_R{}^0$ the resonance effect arising from the substituent in the ground state. Values of $\sigma_I$ are well established for many substituents and can be estimated from aliphatic or aromatic reactivities or from the fluorine n.m.r. shielding parameters for meta-substituted fluorobenzenes. The $\sigma_R{}^0$ values for certain substituents have been found[1,2] both from the difference $\sigma^0 - \sigma_I$, where $\sigma^0$ values have been derived from reactivities, and from the difference in fluorine n.m.r. shielding parameters for para- and meta-substituted fluorobenzenes. Values for substituents capable of conjugative electron withdrawal are found to be solvent dependent and may also be exalted as a result of conjugation with the para-substituted fluorine atom, when determined by the n.m.r. method. The values obtained for such substituents are designated $\bar{\sigma}_R$. Recent work[3] has shown that the carbon-13 chemical shifts of the para carbons in monosubstituted benzenes, especially when corrected by the amount of the corresponding meta shift, correlate closely with $\sigma_R{}^0$ values. This represents the only reported method of measuring such interactions directly.

Although intensities of substituent vibrations have been correlated with $\sigma$ or $\sigma^+$ values,[4] no quantitative relationship for the intensities of the skeletal modes of aromatic molecules has hitherto been established. Katritzky has previously predicted[5] that the intensities of the ring stretching bands in six-membered aromatic

(1) R. W. Taft, Jr., J. Phys. Chem., 64, 1805 (1960), and references given therein.
(2) R. W. Taft, Jr., E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, J. Am. Chem. Soc., 85, 3146 (1963).
(3) G. E. Maciel and J. J. Natterstad, J. Chem. Phys., 42, 2427 (1965), and references given therein.
(4) See, for example, T. L. Brown, J. Phys. Chem., 64, 1798 (1960).
(5) A. R. Katritzky, J. Chem. Soc., 4162 (1958); Quart. Rev. (London), 13, 353 (1959).