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CHEMICALLY INITIATED ELECTRON EXCHANGE LUMINESCENCE. A NEW CHEM--ETC(U)  
MAY 77 G B SCHUSTER, J KOO

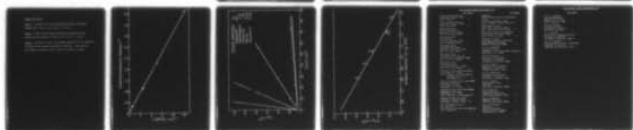
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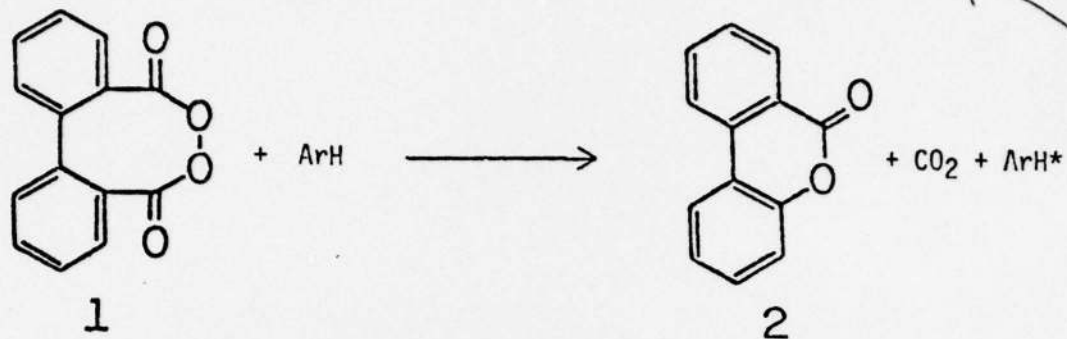
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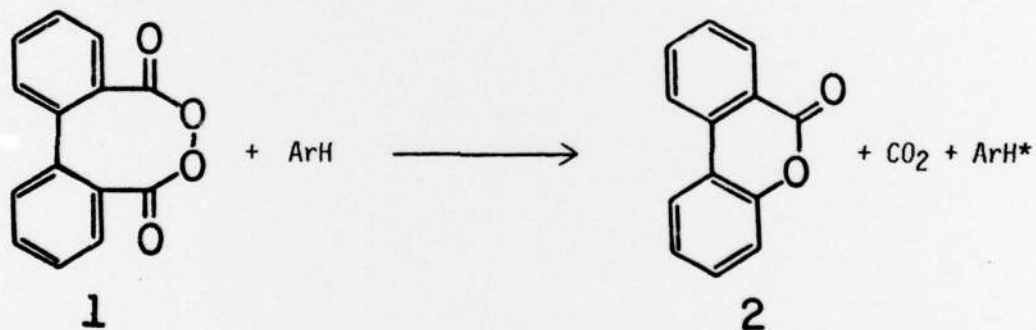
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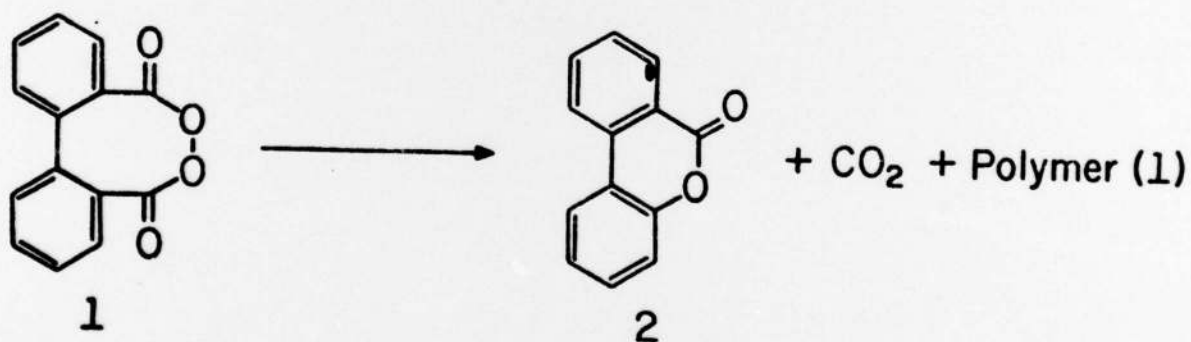
Abstract: The thermal decomposition of diphenylperoxide in the presence of certain aromatic hydrocarbons generates benzocoumarin (2) and light corresponding to the fluorescence spectrum of the hydrocarbon. It is shown that this chemiluminescence does not result from conventional energy transfer from some electronically excited peroxide decomposition product to the aromatic hydrocarbon. Instead, the chemiluminescence is initiated



by electron transfer from the hydrocarbon to the peroxide followed by rapid decarboxylation and back electron transfer to form the electronically excited hydrocarbon. The yield of light from this process is quite high. It is suggested that a similar mechanism may be operating in several previously described chemiluminescing systems.

We would like to report an efficient new chemiluminescent reaction that delineates an apparently important class of chemiluminescent processes and provides insight into several previously reported light producing reactions. In general, the exothermic decomposition of peroxides to directly generate electronically excited state carbonyl compounds has formed the basis for nearly all of organic chemiluminescence.<sup>1</sup> In this communication we will outline a reaction sequence in which diphenylperoxide (1) undergoes chemically initiated electron exchange with an aromatic hydrocarbon to directly form the electronically excited singlet state of the hydrocarbon which, in turn, emits a photon of visible light.

Thermolysis of a dilute solution of diphenylperoxide<sup>2</sup> in  $\text{CH}_2\text{Cl}_2$  at ca.  $24^\circ$  for 24 hr resulted in the formation of benzocoumarin (2) in 75% yield<sup>3</sup> and polymeric peroxide, (equation 1). Under these conditions there was virtually no chemiluminescence from this reaction. However, addition of



certain aromatic hydrocarbons (see Figure 2) to the reaction mixture resulted in efficient light formation. The spectrum of the emission corresponds in all cases to the fluorescence of the added hydrocarbon.

Such an observation is not unique among chemiluminescent systems and has been attributed to electronic energy transfer to the added hydrocarbon from a product molecule formed in an excited state. However, in this case, the unusual



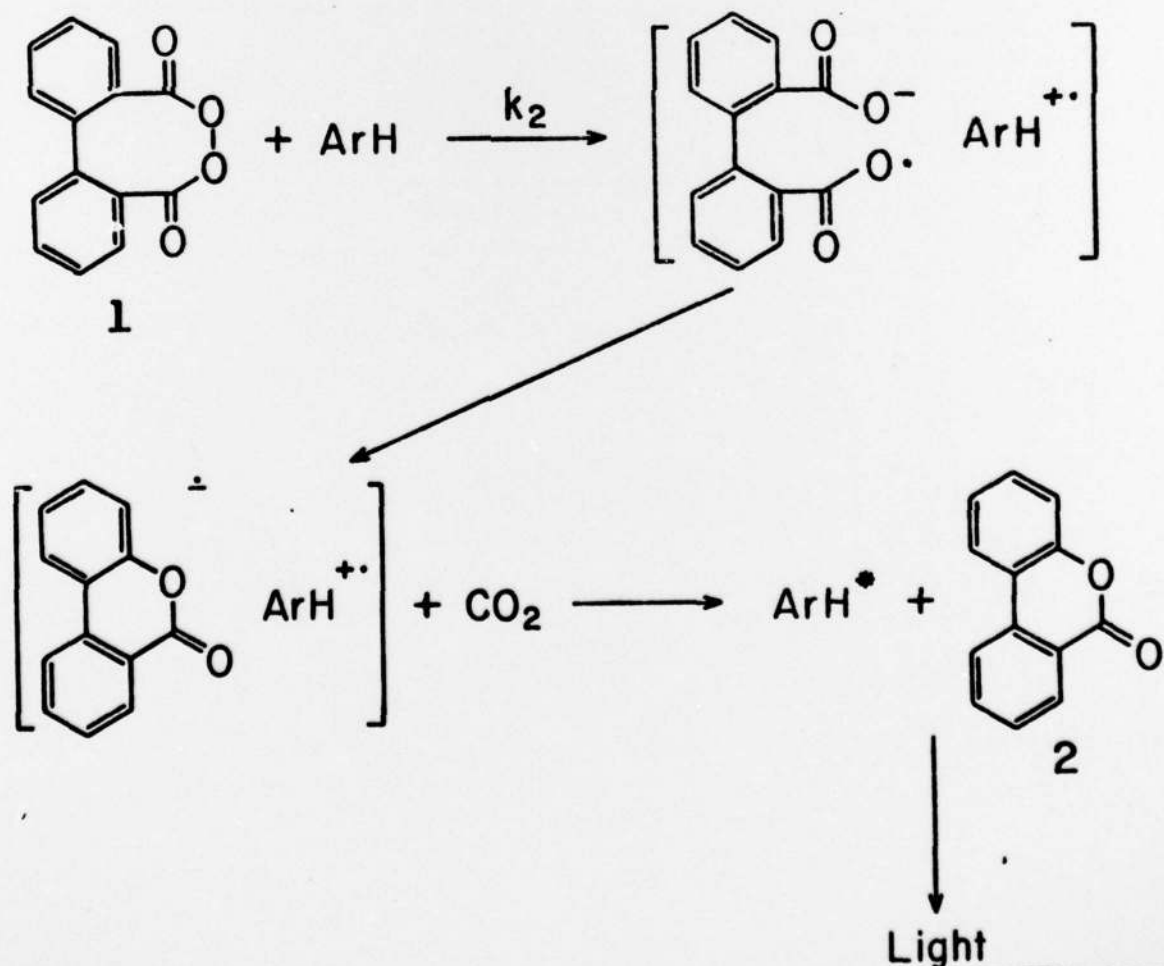
observation was made that while 9,10-diphenylanthracene (DPA) was quite effective at promoting light formation, 9,10-dibromoanthracene and biacetyl were essentially completely ineffective.<sup>4</sup> Moreover, incorporation of the aromatic hydrocarbon in the reaction solution increased the rate of consumption of the diphenylperoxide. These observations indicate a special interaction of the aromatic hydrocarbon with the peroxide rather than simple energy transfer as the light forming step.

The chemiluminescence observed from peroxide  $\downarrow$  and aromatic hydrocarbons is strictly first order in peroxide concentration for more than 5 half-lives. The effect of added aromatic hydrocarbon on the observed rate constant is first order in hydrocarbon and can be represented by a simple kinetic expression, equation 2, where  $k_1$  is the rate constant for the unimolecular reaction and  $k_2$  for the hydrocarbon dependent reaction.

$$k_{\text{obs}} = k_1 + k_2 [\text{Aromatic Hydrocarbon}] \quad (2)$$

Additional evidence that the chemiluminescence is a result of the bimolecular reaction is revealed by the effect of aromatic hydrocarbon concentration on the emitted light intensity. If the unimolecular reaction is responsible for light generation, then at high hydrocarbon concentration, where nearly all of the peroxide reacts by the bimolecular path, the hydrocarbon should act as a quencher of the chemiluminescence. Figure 1, a reciprocal plot of intensity against concentration, shows that the chemiluminescent intensity is a linearly increasing function of the aromatic hydrocarbon concentration even when greater than 90% of the reaction of  $\downarrow$  proceeds through the bimolecular path. Thus, for the cases studied, the formation of light must be a consequence of the reaction of aromatic hydrocarbon with ground state peroxide.

The nature of this interaction was probed by examining the effect of hydrocarbon structure on the rate constant for the bimolecular reaction. Figure 2 shows a plot of the observed first order rate of chemiluminescence decay against hydrocarbon concentration according to equation 2 for a series of hydrocarbons. As predicted by equation 2, all of the hydrocarbons pass through the same intercept ( $k_1$ ), however, the slopes ( $k_2$ ) are strongly dependent on the structure of the hydrocarbon. Figure 3 shows a plot of the natural log of  $k_2$  against the one electron oxidation potential of the aromatic hydrocarbons. The excellent correlation between the observed rate and the oxidation potential indicates that the initiating step in the chemiluminescent process is an electron transfer from the hydrocarbon to the peroxide.<sup>5</sup> In the scheme below, we suggest a mechanism for this chemiluminescent reaction consistent with our observations.



Induced decomposition of peroxidic compounds by nucleophiles<sup>6</sup> and redox metals<sup>7</sup> is well known. Studies of the electrochemical reduction of diacyl peroxides indicate that the electron transfer is irreversible.<sup>8</sup> In the case under study the cage radical ion pair formed by the initial electron transfer from the hydrocarbon to the peroxide has a facile reaction path available. Decarboxylation followed by carbon oxygen bond formation results in the radical anion of benzocoumarin. We have determined that the reduction potential of benzocoumarin is -1.92 eV (vs. SCE).<sup>9</sup> Thus, back electron transfer from the radical anion of  $\overset{\cdot}{\text{C}}\text{O}_2$  to the radical cation of the aromatic hydrocarbon is sufficiently exothermic to generate the electronically excited singlet state of the hydrocarbon. Such reactions have been observed to generate light during electrogenerated chemiluminescence.<sup>10</sup> An important key feature of this new chemiluminescent mechanism is the rapid chemical reaction of what was a very easily reduced compound to form a strongly reducing species within the solvent cage.

The total yield of electronically excited states for this reaction should be sensitive to a number of factors such as the nature of the hydrocarbon, the rate of decarboxylation, the cage lifetime, the solvent polarity, and the excited state yield on back electron transfer. We have compared the chemiluminescence of  $\overset{\cdot}{\text{C}}\text{O}_2$  with perylene to tetramethyldioxetane.<sup>11</sup> Preliminary results indicate that for this system the yield of photons is ca.  $10 \pm 5\%$ . Thus, even though the reaction has not been optimized, the light yield is remarkably high.

Several previously reported chemiluminescent reactions appear to be proceeding by the proposed electron exchange mechanism. The well known oxalate ester system is reported to be "catalyzed" by aromatic hydrocarbons.<sup>13</sup> Chemiluminescence from  $\alpha$ -peroxylactones appears to be strongly dependent upon the nature of the aromatic hydrocarbon.<sup>14</sup> The reaction of phthaloyl

peroxide almost certainly proceeds by the proposed mechanism.<sup>15</sup> Our recent report of chemiluminescence from a suspected cyclic diacyl peroxide fits this interpretation.<sup>16</sup> Chemically initiated electron exchange luminescence may be a general phenomenon responsible for many chemi- and bioluminescent reactions. Further efforts to unravel the details of these chemiluminescent processes and probe the generality of this mechanism are underway.

Acknowledgement. We wish to thank Professor Faulkner of this Department for the determination of the reduction potential of benzocoumarin and for many helpful discussions. This work was supported in part by the Office of Naval Research and in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

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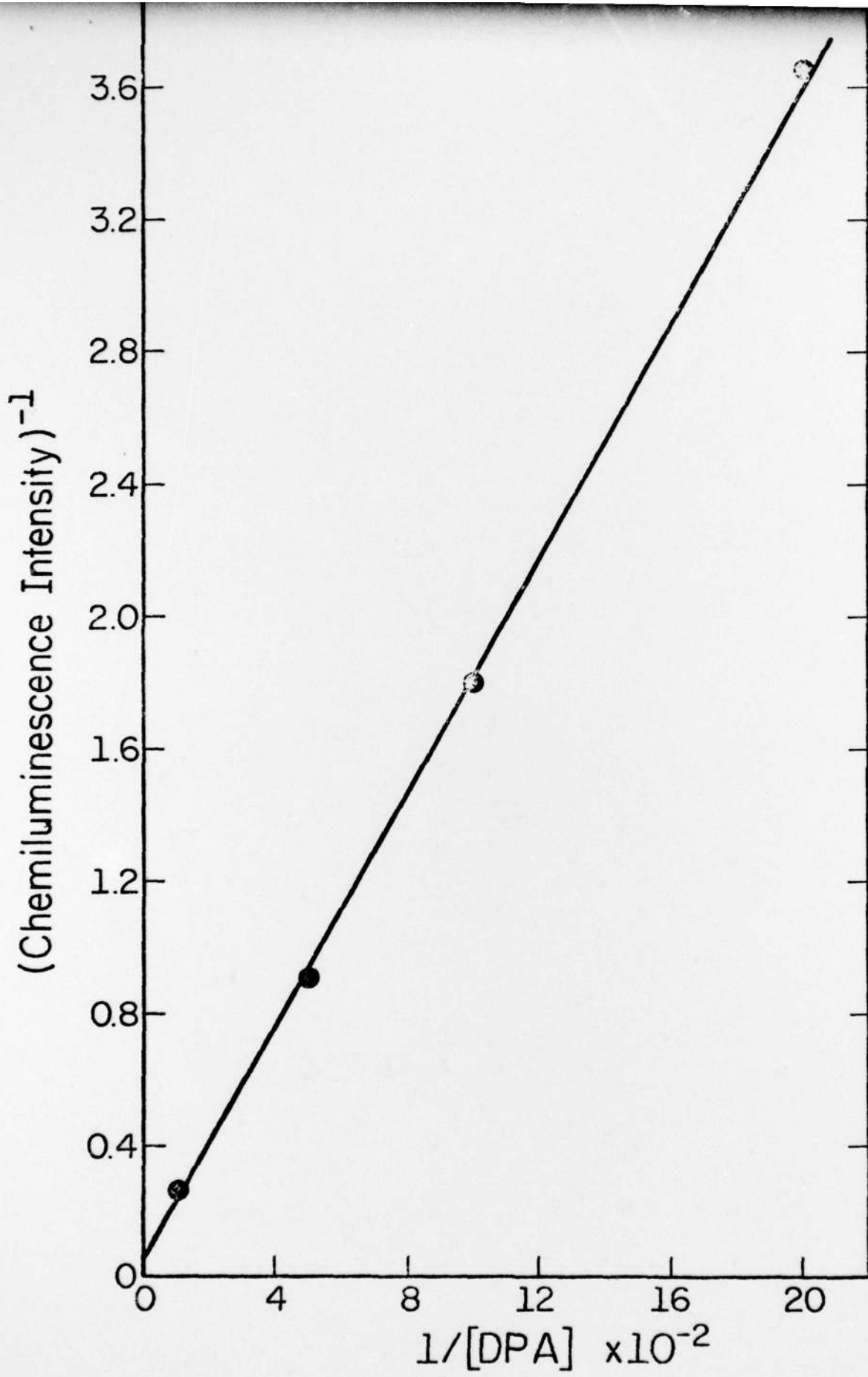
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Captions for Figures

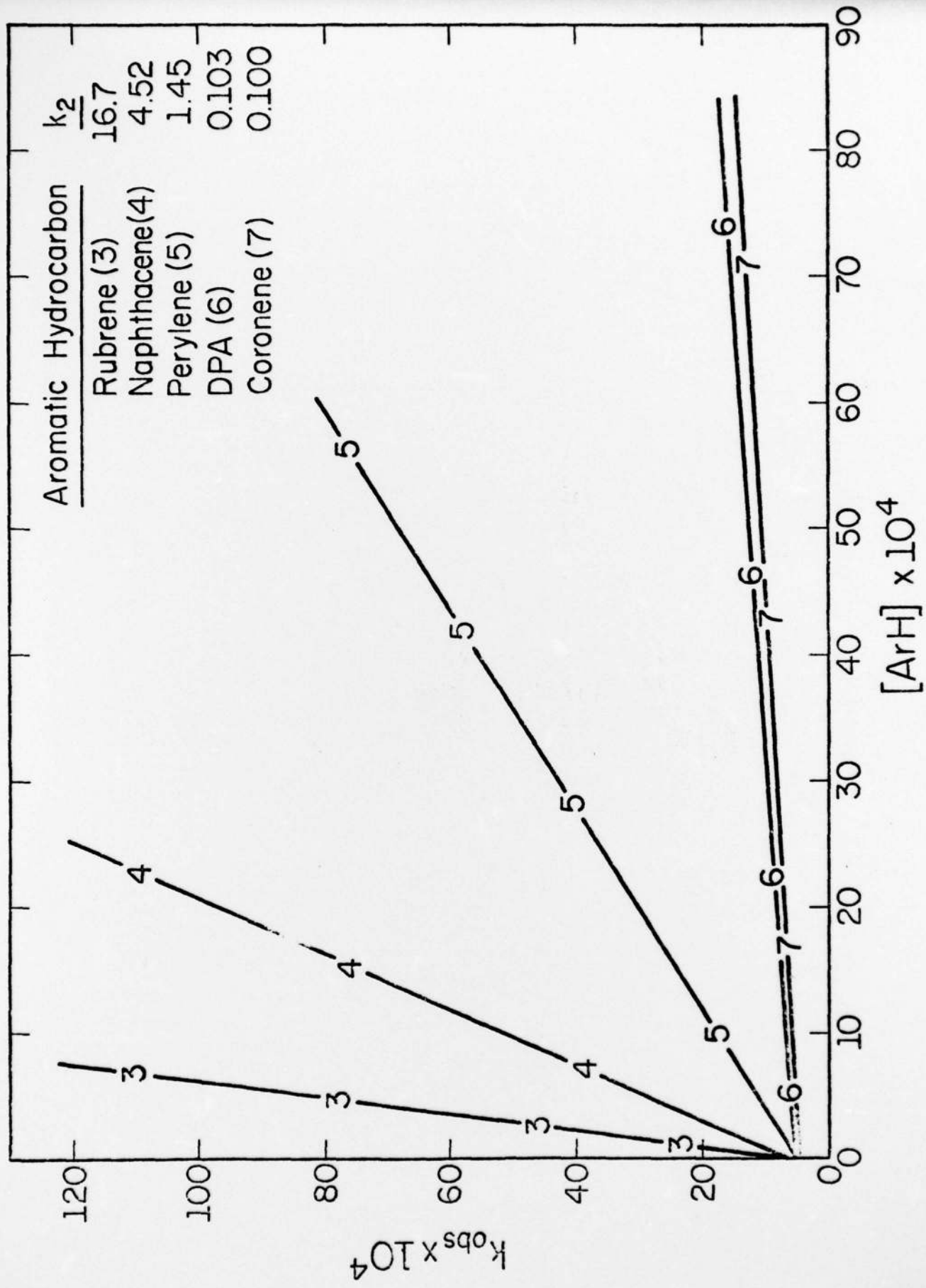
Figure 1. Reciprocal plot of chemiluminescence intensity against DPA concentration in  $\text{CH}_2\text{Cl}_2$  at  $32.5^\circ$ ;  $[\text{I}] = 5 \times 10^{-5} \text{ M}$ .

Figure 2. Effect of added aromatic hydrocarbon concentration on the reaction rate for peroxide  $\text{I}$  in  $\text{CH}_2\text{Cl}_2$  at  $32.5^\circ$ ;  $[\text{I}] = 5 \times 10^{-5} \text{ M}$ .

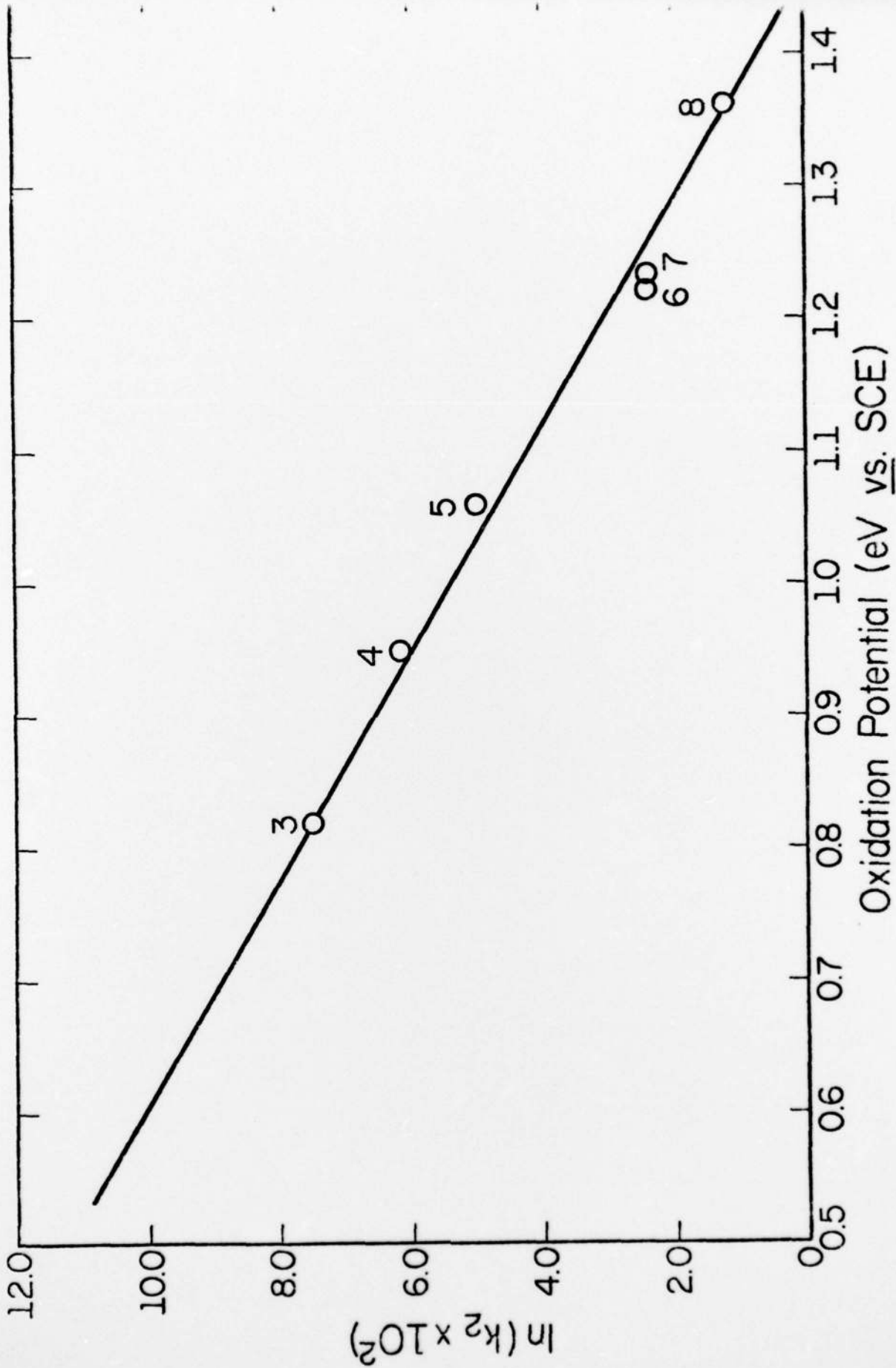
Figure 3. Correlation of  $\log k_2$  and oxidation potential<sup>17</sup> for the chemically initiated electron exchange luminescence of peroxide  $\text{I}$ . Note that the point numbers correspond to those in Figure 2 and that  $\text{g}$  is pyrene.







[ArH] x 10 <sup>4</sup>	k <sub>obs</sub> x 10 <sup>4</sup> (Series 3)	k <sub>obs</sub> x 10 <sup>4</sup> (Series 4)	k <sub>obs</sub> x 10 <sup>4</sup> (Series 5)	k <sub>obs</sub> x 10 <sup>4</sup> (Series 6)	k <sub>obs</sub> x 10 <sup>4</sup> (Series 7)
0	0	0	0	~10	~10
10	~10	~20	~30	~10	~10
20	~20	~40	~60	~10	~10
30	~30	~60	~90	~10	~10
40	~40	~80	~120	~10	~10
50	~50	~100	~150	~10	~10
60	~60	~120	~180	~10	~10
70	~70	~140	~210	~10	~10
80	~80	~160	~240	~10	~10
90	~90	~180	~270	~10	~10



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