

dimers and that c_h in the presence of air is only about 8×10^{-3} M.

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DR. SELINGER has directed attention to an unintentional ambiguity in our original communication. In comparing the fluorescence spectrum Z of the mixed solution, containing equimolar concentrations of A and B , with the sum ($A + B$) of the fluorescence spectra of the two separate solutions of A and B , the relative quantum intensities of the monomer components of Z and ($A + B$) were normalized. Reference to this standard procedure, which has been followed in other reports¹ of excimer fluorescence spectra from these laboratories, was unfortunately omitted. The ratio of the quantum yield of excimer fluorescence I_D to that of monomer fluorescence I_M is given by²:

$$\frac{I_D}{I_M} = \frac{q_{DC}}{q_M c_h}$$

where c is the molar concentration, c_h is the 'half-value' concentration, and q_M and q_D are the monomer and excimer fluorescence quantum efficiencies at $c = 0$ and $c = \infty$, respectively. For the normalized spectra, the excimer fluorescence intensity is proportional to I_D/I_M and hence to c . For the unnormalized spectra, I_D and I_M vary non-linearly with c , according to the Stern-Volmer relations². Our original data³, prior to normalization, agree closely with those reported by Selinger. They substantiate the conclusion, implicit in our previous communication, that mixed dimers of similar compounds are formed with the same probability and fluorescence quantum efficiency as the pure dimers.

J. B. BIRKS

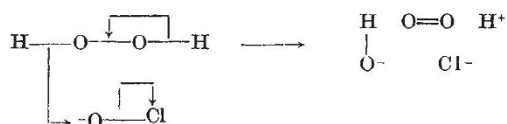
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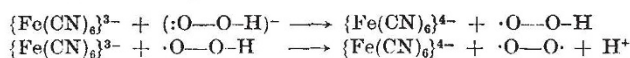
Chemi-luminescence as a Diagnostic Feature of Heterolytic Reactions which Produce Oxygen

THE recent suggestions by Khan and Kasha¹ and by Ogryzlo *et al.*² that the emission of light which occurs during the interaction of hydrogen peroxide and sodium hypochlorite might be ascribed to singlet triplet transitions of molecular oxygen have led us to examine the possibility that among those chemical reactions which yield molecular oxygen the heterolytic processes alone might prove to be chemi-luminescent.

By electron-pair movements, for example:



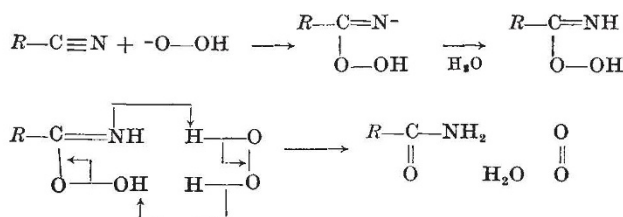
oxygen should initially be formed in a diamagnetic singlet state, whereas in reactions involving one-electron movements, for example:



the oxygen should be formed in a di-radical, or triplet, state. Suggestions that heterolytic reactions might initially give activated forms of singlet oxygen, or that singlet-triplet transitions of molecular oxygen may need two oxygen molecules, are both irrelevant to this simple mechanistic differentiation between the two contrasting types of oxygen-producing reactions.

With the help of Dr. E. J. Bowen, who has put a sensitive photomultiplier at our disposal, we have found that other heterolytic oxygen-producing reactions are indeed chemi-luminescent.

While from the NaOCl—H₂O₂ reaction there is a short-lived emission of red light, from admixture of chloramine- T with neutral hydrogen peroxide the emitted light has both red and blue components. Singlet oxygen is formed in the reaction between alkaline hydrogen peroxide and nitriles; the mechanism of this³ can be represented as:



When benzyl cyanide was used with 30 per cent hydrogen peroxide in alcoholic potassium hydroxide a bluish light, strong enough for visual observation in a darkened room, was emitted for 5–10 min. Examination with a photomultiplier and a red filter (Ilford 204) showed that this had a small red component. Acrylonitrile also gave strong emission of blue light, but with benzonitrile the emission was just detectable with the photomultiplier. A transient emission of light was also observed during the interaction of hydroxylamine with alkaline hydrogen peroxide.

No emission of radiation could be detected during the oxygen-producing reactions between hydrogen peroxide and KMnO₄, MnO₂, K₃Fe(CN)₆ and Ce(SO₄)₂, which are all one-electron-transfer processes.

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Temperature Variation of β-Type Interlamellar Sorption Complexes of Graphitic Acid with Alcohols

FURTHER investigations have been made of the β-type interlamellar sorption complexes formed by graphitic acid with normal alcohols^{1–3}. We find that the formation of β-complexes (chain perpendicular to layer) or α-complexes (chain parallel to layer) with any given alcohol depends on the method of formation and pretreatment of the graphitic acid⁴. We have evidence that this statement may be true also for the α- and β-complexes of montmorillonite.

For the work recorded here, we selected one of the 'best' acids (that is, forming β-complexes most easily). We used a sample of graphitic acid dried at ambient temperature, and the same sample dried at 65° C. The complexes formed were examined by X-ray diffraction at ambient temperature, at +70° C and at -50° C. Results, in the form of a graph of basal spacing versus chain-length, are shown in Fig. 1.