

Of course $N > N_0$, and $N_0 = 17$ (ref. 14) from our chosen value of P'_0/a (but see ref. 15). N_0 and N are, however, sensitive to changes in P'_0/a and might be substantially different for borazoles or cyclic azines.

It must be recognized that a more refined treatment of this question would need also to include: mixing in of d_{yz} character (in Craig's notation); the effect of non-planarity; and also the participation of lone-pair electrons (' π' -bonding')¹⁶.

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¹ Davies, D. W., *Nature*, **194**, 82 (1962).² Longuet-Higgins, H. C., and Salem, L., *Proc. Roy. Soc., A*, **251**, 172 (1959).³ a, Craig, D. P., *Proc. and Disc. Kekulé Symposium*, 21 (Butterworths, 1959); b, *J. Chem. Soc.*, 997 (1959).⁴ See also Dewar, M. J. S., Lucken, E. A. C., and Whitehead, M. A., *J. Chem. Soc.*, 2423 (1960).⁵ Functional forms for $\beta(r)$ and $P(r)$ different from those chosen in ref. 2 do not affect the main conclusions of the theory (Haigh, C. W., to be published).⁶ Davies, quoting Coulson, ref. 7, wrote $\partial^2 E/\partial x^2 = n^2$; but the latter wrote $\partial^2 E/\partial r_1^2 = n^2$, without assuming $r_1 + r_2 = 2r_0$.⁷ Coulson, C. A., *Tetrahedron*, **12**, 393 (1961).⁸ Salem, L., and Longuet-Higgins, H. C., *Proc. Roy. Soc., A*, **255**, 435 (1960).⁹ Lennard-Jones, J. E., and Turkevich, J., *Proc. Roy. Soc., A*, **158**, 301 (1937).¹⁰ See Gouterman, M., and Wagnière, G., *J. Chem. Phys.*, **36**, 1192 (1962) for C_2H_4 , and particularly Fig. 5.¹¹ Longuet-Higgins, H. C., *Proc. and Disc. Kekulé Symposium*, 17 (Butterworths, 1959).¹² Shaw, R. A., Fitzsimmons, B. W., and Smith, B. C., *Chem. Revs.*, **62**, 275 (1962). For $(PNCl_2)_3$ we place greater reliance on Wilson, A., and Carroll, D. F., *J. Chem. Soc.*, 2548 (1960), than on Giglio, E., *Ricerca Sci.*, **30**, 721 (1960).¹³ Chapman, A. C., and Paddock, N. L., *J. Chem. Soc.*, 635 (1962). Chapman, A. C., quoted in ref. 16c.¹⁴ The use of more recent bond-lengths [see, for example, Coulson, C. A., and Golebiewski, A., *Proc. Phys. Soc., A*, **78**, 1315 (1961)] does not affect these figures.¹⁵ Longuet-Higgins, H. C., and Salem, L., *Proc. Roy. Soc., A*, **257**, 445 (1960).¹⁶ a, Craig, D. P., Heffernan, M. L., Mann, R., and Paddock, N. L., *J. Chem. Soc.*, 1376 (1961), especially Table 1 and Fig. 1. b, Cruickshank, D. W. J., *J. Chem. Soc.*, 5501 (1961). c, Craig, D. P., and Paddock, N. L., *J. Chem. Soc.*, 4118 (1962).

I AM indebted to Mr. Haigh and Dr. Salem for pointing out the mistake in my communication. They correctly state that $E_{xx}^n \rightarrow \infty$ as $n \rightarrow \infty$, and that the infinite heterocyclic ring can have, respectively, equal or unequal bond-lengths depending on whether δ is greater or smaller than a critical value.

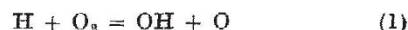
The other conclusions of my communication are not affected by this mistake, and they are confirmed by Mr. Haigh and Dr. Salem. I confined myself to the cyclic phosphazenes, and treated them as heteromorphic systems. This gave the interesting result that bond alternation might occur below a critical value of n . Mr. Haigh and Dr. Salem consider other possibilities implicit in my equation (9), and show that, for suitable values of δ , odd homomorphic heterocyclic rings can behave like homocyclic rings, with bond alternation occurring above a critical value of n . In particular, they show that treating the known cyclic phosphazenes as odd homomorphic systems does not affect my result that bond alternation should not occur.

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Role of Hydroperoxyl in Hydrogen-Oxygen Flames

THE hydroperoxyl radical has been postulated as an intermediate in numerous oxidation reaction mechanisms. In particular, mechanisms involving it are capable of giving detailed explanations of the explosion limits and reaction-rates in hydrogen-oxygen systems in static reaction vessels^{1,2}. In discussing hydrogen-oxygen and hydrogen-air flames, however, reactions of HO_2 are usually omitted, on the assumption that most of the flame reaction occurs at too high a temperature for the HO_2 forming reaction (2) to compete with the chain-branching reaction (1).



We have recently obtained evidence, arising from a detailed investigation of a slow-burning hydrogen-oxygen-nitrogen flame and from calculations involving two faster (higher temperature) flames, that this assumption may be invalid in many cases.

The atmospheric pressure flame selected for detailed examination had a final temperature of 1,072° K and a burning velocity of 9.2 cm sec⁻¹ (gas flows measured at 18° C and 760 mm). The initial gas temperature was 336° K. Analysis of the measured temperature profile gave a maximum heat release-rate of 20 (± 2) cal cm⁻³ sec⁻¹ at 900° K, while the maximum hydrogen atom concentration, measured by studying the rate of the H + D₂ exchange reaction in the flame, was about 2.5 $\times 10^{-8}$ mole cm⁻³ at this temperature. Further, at 900° K (O_2) ~ 1 , (H_2) ~ 11.3 and (H_2O) ~ 7.2 mole per cent.

Now the second limits of hydrogen-oxygen mixtures in potassium chloride coated reaction vessels at temperatures up to about 850° K are normally assumed to be ultimately controlled by a competition between reactions (1) and (2). At the limit the partial pressures of the reactants and inert gases obey the relationship $2k_1/k_2H_2 = (H_2) + k_{O_2}(O_2) + k_M(M)$, where k_M denotes the efficiency of molecule M (relative to hydrogen) as the third body in reaction (2). Clearly, the ratio $2k_1/k_2H_2$ may be found from a study of the variation of the second limit with mixture composition. A short extrapolation of the Arrhenius plot for this ratio from second limit data leads to $k_1/k_2H_2 = 150$ mm at 900° K. Second limit data³⁻⁵ also show that $k_2N_2 = 0.45k_2H_2$ and $k_2H_2O \sim 6.5k_2H_2$. For the flame composition at atmospheric pressure it might therefore be expected that reaction (2) is some four to four and a half times as fast as reaction (1), that is, that HO_2 reactions are important at the position of maximum reaction-rate. This conclusion is supported by a simple calculation of the heat release-rate in the flame using the experimental concentration values. In the absence of HO_2 forming reactions, and using $k_1 = 2.1 \times 10^{10}$ cm³ mole⁻¹ sec⁻¹, at 900° K (a value which is consistent with the recent literature⁶), together with recent experimental values⁶ for the hydrogen atom recombination rate constant, a maximum heat release-rate of about 3 cal cm⁻³ sec⁻¹ is obtained (cf. experimental 20 cal cm⁻³ sec⁻¹). Similarly, the measured rate of oxygen consumption in the flame is some four to five times larger than would be predicted from the foregoing value of k_1 . It seems highly likely, therefore, that much of the reaction path in this flame is by way of HO_2 .

By making the assumption that the HO_2 concentration assumes a kinetic steady state value, it is