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 $\partial^2 E^\sigma / \partial x^2 = nf''$; but the latter wrote $\partial^2 E^\sigma / \partial r_1^2 = nf''$, 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 $C_{24}H_{24}$, 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. 16*c*.

[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).

$$H + O_2 = OH + O \qquad (1)$$

$$H + O_2 + M = HO_2 + M \qquad (2)$$

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 $H + D_2$ exchange reaction in the flame, was about $2{\cdot}5 \times 10^{-8}$ mole cm^{-3} at this temperature. Further, at 900° K $(O_2) \sim 1$, $(H_2) \sim 11{\cdot}3$ and $(H_2O) \sim 7{\cdot}2$ 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 data[3–5] also show that $k_{2N_2} = 0{\cdot}45 k_{2H_2}$ and $k_{2H_2O} \sim 6{\cdot}5 k_{2H_2}$. 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 $k_1 = 2{\cdot}1 \times 10^{10}$ cm^3 $mole^{-1}$ sec^{-1}, at 900° K (a value which is consistent with the recent literature[5]), together with recent experimental values[6] 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 possible to make an estimate of the HO_2 concentration in the part of the flame near the maximum reaction-rate and also to suggest its main reaction path. Work[1,2] on the hydrogen–oxygen slow reaction and explosion limits suggests that reactions (3)–(6) may have to be considered as steps consuming HO_2.

$$HO_2 + H_2 = H_2O_2 + H \qquad (3)$$

$$HO_2 + H_2O = H_2O_2 + OH \qquad (4)$$

$$H + HO_2 = OH + OH \qquad (5)$$

$$HO_2 + HO_2 = H_2O_2 + O_2 \qquad (6)$$

The ratios of rate constants $k_3^2/k_6 = 0{\cdot}96$ cm^3 mole^{-1} sec^{-1} and $k_5^2/k_6k_2^2 = 1{\cdot}2 \times 10^{-4}$ mole cm^{-3} sec at 500° C have been derived by Baldwin and Mayor[1] on the basis of reaction mechanisms which satisfactorily interpret in detail the features of the hydrogen–oxygen reaction in aged boric acid coated vessels at that temperature. Taking $k_2 = 4{\cdot}7 \times 10^9$ at 500° C, $k_5^2/k_6 = 2{\cdot}6 \times 10^{15}$ cm^3 mole^{-1} sec^{-1}, a value only slightly less than the ratio $Z_5^2/Z_6 = 4{\cdot}8 \times 10^{15}$ quoted by Baldwin and Mayor. Foner and Hudson[7] have recently obtained $k_6 = 1{\cdot}8 \times 10^{12}$ cm^3 mole^{-1} sec^{-1} at room temperature, using mass spectrometry to measure HO_2 concentrations. Further, the very reasonable inclusion of reactions (5) and (6) in the mechanism proposed by Burgess and Robb[8] for the mercury photosensitized reaction of hydrogen and oxygen at room temperature would require the activation energy E_6 to be low, regardless of the actual value of k_6. Taking $E_6 = 0$, the values $k_3 = 1{\cdot}3 \times 10^6$ and $k_5 = 6{\cdot}9 \times 10^{13}$ cm^3 mole^{-1} sec^{-1} at 500° C then result.

An alternative value for k_6 ($= 6{\cdot}5 \times 10^{13}$ cm^3 mole^{-1} sec^{-1} at about 30° C, and implying a collision efficiency close to unity for both reactions (5) and (6)) has been derived by Burgess and Robb[8] in the work already quoted. For reaction (6) such a high collision efficiency seems to us to be somewhat surprising. Taking $E_6 = 0$, it would lead to $k_3 = 7{\cdot}9 \times 10^6$ and $k_5 = 4{\cdot}1 \times 10^{14}$ at 500° C. It should be noted also that both values of k_3 are more than 50 times greater than a third value[9-11] of $1{\cdot}2 \times 10^{11} \exp(-24{,}000/RT)$, giving $k_3 = 2{\cdot}2 \times 10^4$ at 500° C, due to Voevodsky and Tal'Rose[10], and derived from slow reaction and third limit studies of the hydrogen–oxygen system in vessels coated with potassium chloride. In view of the more recent developments in connexion with the hydrogen–oxygen system, values derived from older third limit mechanisms may be open to question.

In the flame at 900° K, $(H)/(H_2) \approx 10^{-3}$ and, for $E_3 - E_5 \approx 25$ kcal mole^{-1}, $k_5(H)/k_3(H_2)$ has a minimum value of the order of 10^4. Reaction (3) is therefore unimportant in this region of the flame. Reaction (4), which is endothermic to the extent of about 29 kcal mole^{-1}, is also unlikely appreciably to affect the kinetics. The main reaction path for the HO_2 is therefore most likely to be via reactions (5) and (6), which together with the HO_2 forming reaction (2) would lead to a kinetic steady state concentration $(HO_2) \sim 8 \times 10^{-10}$ mole cm^{-3} (or about one-thirtieth of the hydrogen atom concentration), if Foner and Hudson's value for k_6 is used, or $(HO_2) \sim 1{\cdot}3 \times 10^{-10}$ mole cm^{-3} using Burgess and Robb's value. Further, the rates of reactions (5) and (6) at 900° K in the flame may now be compared approximately. The ratio, using either value of k_6, is:

$$\frac{R_5}{R_6} = \frac{k_5(H)}{k_6(HO_2)} \approx 1{,}200$$

It therefore seems that reaction (5) provides the main reaction path, and that HO_2 concentration in the flame is considerably smaller than the hydrogen atom concentration. The figures quoted depend, of course, on the kinetic steady state assumption, which is not strictly true in the flame due to the diffusion and gas flow processes. A more accurate numerical calculation will be published in due course.

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[1] Baldwin, R. R., and Mayor, L., *Trans. Farad. Soc.*, **56**, 80, 103 (1960).

[2] Baldwin, R. R., Doran, R., and Mayor, L., *Trans. Farad. Soc.*, **56**, 93 (1960).

[3] Dixon-Lewis, G., and Linnett, J. W., *Trans. Farad. Soc.*, **49**, 756 (1953).

[4] Ashmore, P. G., and Tyler, B. J., *Trans. Farad. Soc.*, **58**, 1108 (1962).

[5] Baldwin, R. R., and Brooks, C. T., *Trans. Farad. Soc.*, **58**, 1782 (1962).

[6] Dixon-Lewis, G., Williams, A., and Sutton, M. M., *Disc. Farad. Soc.* (in the press).

[7] Foner, S. N., and Hudson, R. L. (private communication).

[8] Burgess, R. H., and Robb, J. C., *Spec. Pub. Chem. Soc.*, No. 9, 167 (1957).

[9] Kondriatiev, V. N., *Doklady Akad. Nauk. S.S.S.R.*, **137**, 120 (1961).

[10] Voevodsky, V. V., and Tal'Rose, V. L., *Zh. fiz. Khim.*, **22**, 1192 (1948).

[11] Voevodsky, V. V., *Seventh Symp. on Combustion*, 34 (Butterworths, London, 1959).

Determination of the Adsorption of Ethylene on Platinum Electrodes using a Radiotracer Method

THERE has been a recent surge of interest in the mechanism of the electrochemical oxidation of hydrocarbons. Important to any determination of mechanism is a knowledge of the fractional surface coverage of reaction species. This communication deals with the adsorption of ethylene labelled with carbon-14 at the platinum-electrolyte interface as a function of potential and time.

The method for measuring the electrode surface concentration of carbon-14 containing species under electrochemically controlled conditions consists basically in an adaptation of the Joliot method[1,2]. In this work the electrode under study is a thin metal foil (10^4 Å thick), which is placed over the window of a proportional counter (suitable for detecting weak β-rays). The electrode is brought into contact with the solution, and from the count rate, after suitable calibration, it is possible to determine the surface concentration of carbon-14 and from that the surface

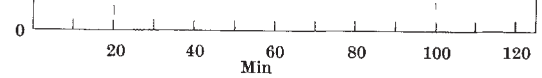

Fig. 1. Time dependence of adsorption and desorption at constant potentials. Potentials *E* are expressed against the normal hydrogen electrode