82. *Bond Energies in Peroxides, and the Energy evolved in the Reaction* $H + O_2 = HO_2$.

By A. D. Walsh.

The bond energies in hydrogen peroxide, organic peroxides, and the radical HO_2 are considered. Many reasons are given why a recent estimate by Glockler and Matlack of the OO bond energy in hydrogen peroxide appears too low: the true value is considered to be ~ 64 kcals./mole, and the OO dissociation energy in the same molecule is ~ 56 kcals./mole. In organic peroxides the indications are that, other things being equal, the OO bond strength increases with increasing transfer of negative charge to the bond: an explanation of this in terms of increased " overlap " is offered. Various lines of evidence point to the fact that the energy evolved in the gas reaction $H + O_2 = HO_2$ is greater than has usually been supposed: a value ~ 60 kcals./mole or more seems more probable than one in the range 40—50 kcals./mole. In other words, HO_2 in its ground state is likely to be more inert than has previously been supposed.

The vast importance of peroxides in many fields of chemistry is now recognised. Knowledge of their properties is still meagre in the extreme. The following notes attempt to add a little to the as yet rudimentary understanding of peroxide thermochemistry. They also consider the energy evolved in the reaction $H + O_2 = HO_2$. This reaction is of fundamental importance for the theory of the hydrogen–oxygen reaction and indeed of oxidations in general. Although the radical has frequently been invoked to explain reactions, there has been no commensurate consideration of its heat of formation, though a knowledge of this quantity is essential in deciding the probability of the postulated reactions. We begin by considering the bond strengths in the hydrogen peroxide molecule.

Bond Strengths in Hydrogen Peroxide.—Pauling (" Nature of the Chemical Bond ", Cornell, 1940) assumed the OH bond strengths in water and hydrogen peroxide to be identical (110 kcals./mole): in consequence, from thermal data, he derived the value 35 kcals./mole for the OO bond energy in hydrogen peroxide. Skinner (*Trans. Faraday Soc.*, 1945, **41**, 645), on the basis of consideration of various resonance structures, decided that the OH bond was weaker in hydrogen peroxide than in water and consequently arrived at the value 52 kcals./mole for the OO bond energy. Glockler and Matlack (*J. Chem. Physics*, 1946, **14**, 504) have recently argued that Pauling's value is to be preferred to that of Skinner. Evidence is now cited that the true value is even higher than that of Skinner.

We shall use the term " bond energy " to mean an energy quantity characteristic of the bond as it actually exists in the equilibrium state of the molecule: it is chosen (Walsh, *Trans. Faraday Soc.*, 1947, **43**, 60; *J.*, in course of publication) in such a way that (*a*) the sum of the bond energies is equal to the heat of atomisation of the molecule with respect to those atomic states that correspond to the valencies of the atoms of the molecule, and (*b*) it serves as a parameter for the interconversion of such bond properties as force constant, length, ionisation potential, etc., standard points for the relation of bond energy to these properties being provided by molecules where all the bonds are the same. The peroxide bond energy in hydrogen peroxide will not be the same as the bond *dissociation energy*, since the OH bonds in the molecule are not identical with that in the free OH radical. Glockler and Matlack do not distinguish between bond and dissociation energy. Bichowsky and Rossini's data for the heat of formation of gaseous hydrogen peroxide being accepted, then, as Skinner showed, the heat of atomisation is 255·7 kcals. Since the dissociation energy of the OH radical is ~ 100 kcals. (Dwyer and Oldenberg, *J. Chem. Physics*, 1944, **12**, 351), the dissociation energy of the OO bond in hydrogen peroxide follows unambiguously as ~ 56 kcals.

In three papers (Walsh, *Trans. Faraday Soc.*, 1946, **42**, 56; 1947, **43**, 60, 158), it has been shown, mainly from a study of the ionisation potentials of non-bonding electrons, that the more polar a given bond the weaker it is, *i.e.*, the less its stretching force constant and bond energy and the greater its length. This fact means that the resonance description of bond polarity as due to ionic–covalent resonance is only helpful in assessing the bond energies in hydrogen peroxide if supplemented by discussion of the energies of stretching and compression of bonds (Walsh, *Ann. Reports*, in the press).

Since the oxygen atom in water has two hydrogen atoms on which to expend its electron attraction, whereas in the OH radical it has only one, we expect the electrons of the bond in the OH radical to be more polarised than those in the OH bond of the water molecule. The dipole in each bond of H_2O tends to reduce that in the other bond. Hence, if E and D signify bond and dissociation energy respectively,

$$D(\mathrm{H{-}OH})_{\mathrm{H_2O}} > E(\mathrm{O{-}H})_{\mathrm{H_2O}} > E(\mathrm{O{-}H})_{\mathrm{OH\ rad.}}$$

—an expectation fully confirmed by the facts: $D(\mathrm{H{-}OH})_{\mathrm{H_2O}} = 118$ kcals. (Dwyer and Oldenberg, *loc. cit.*), $E(\mathrm{O{-}H})_{\mathrm{OH\ rad.}} = 100$ kcals., and $E(\mathrm{O{-}H})_{\mathrm{H_2O}} = 110$ kcals. The weakness of the bond in the OH radical is shown further in its length (r) and stretching force constant (k) : $r(\mathrm{OH})_{\mathrm{OH\ rad.}} = 0{\cdot}971$ A. (Herzberg, " Molecular Spectra and Molecular Structure ", Prentice Hall, 1939), $r(\mathrm{OH})_{\mathrm{H_2O}} = 0{\cdot}955$ A. (*idem*, " Infra-red and Raman Spectra ", Van Nostrand, 1945); $k(\mathrm{OH})_{\mathrm{OH\ rad.}} = 7{\cdot}12 \times 10^5$ dynes/cm., $k(\mathrm{OH})_{\mathrm{H_2O}} = 7{\cdot}66 \times 10^5$ dynes/cm. (*idem.*, 1945, *loc. cit.*).

Now the attachment of the electronegative (OH) group to the O atom of a hydroxyl group must make the bond in that hydroxyl group more polar; *i.e.*, the OH bond in the hydrogen peroxide molecule must be slightly more polar and therefore slightly weaker than the bond in the OH radical. Confirmation of this is to be seen in (*a*) the OH length reported by Giguère (quoted in *Chem. Abs.*, 1946, **40**, 1072) for hydrogen peroxide: $r(\mathrm{OH})_{\mathrm{H_2O_2}} = 1{\cdot}01 \pm 0{\cdot}03$ A., $r(\mathrm{OH})_{\mathrm{OH\ rad.}} = 0{\cdot}97$ A.; (*b*) the OH bond stretching force constant reported (Bailey and Gordon, *Trans. Faraday Soc.*, 1938, **34**, 1133) for hydrogen peroxide: $k(\mathrm{OH})_{\mathrm{H_2O_2}} = 6{\cdot}5 \times 10^5$ dynes/cm., $k(\mathrm{OH})_{\mathrm{OH\ rad.}} = 7{\cdot}1 \times 10^5$ dynes/cm. We therefore have strong grounds, from several different sources, for asserting that the OH bond energy in hydrogen peroxide must be a few kcals. *below* the strength in the OH radical (100 kcals./mole).

From the heat of atomisation, the expectation that $E(\mathrm{OH})_{\mathrm{H_2O_2}}$ must be less than 100 kcals. means a lower limit of 56 kcals. for $E(\mathrm{OO})_{\mathrm{H_2O_2}}$. If we choose a value $\sim$ 96 kcals. for $E(\mathrm{OH})_{\mathrm{H_2O_2}}$, we obtain $\approx$ 64 kcals. for the OO bond energy in hydrogen peroxide. Some confirmation of this choice may be seen as follows:

(1) The expected sequence

$$E(\mathrm{Se{-}Se}) < E(\mathrm{S{-}S}) < E(\mathrm{O{-}O})$$

accords well with values for $E(\mathrm{O{-}O})$ in the range 56—70, since $E(\mathrm{Se{-}Se})_{\mathrm{Se_6}}$ is 41 kcals. and $E(\mathrm{S{-}S})_{\mathrm{S_8}}$ is 54 kcals. (Skinner, *loc. cit.*).

(2) Though the precise value for $E(\mathrm{O{-}O})$ will depend upon the particular peroxide in which the peroxide bond is situated, the variation will not be great. The value found by Bolland and Gee (*Trans. Faraday Soc.*, 1946, **42**, 244) for the OO dissociation energy of a hydroperoxide of type $\mathrm{R{\cdot}CH{:}CH{\cdot}CH(O{\cdot}OH){\cdot}R}$ is 66 kcals., and the dissociation energy of the OO bond in persulphates is 57 kcals. (Palmer, " Valency ", Cambridge, 1944). Since E is probably not far different from D in these compounds, these values may be said to support the range of our choice for $E(\mathrm{OO})_{\mathrm{H_2O_2}}$.

(3) Although elsewhere (Long and Walsh, *Trans. Faraday Soc.*, 1947, **43**, 342) we have criticised the over-rigid application of the empirical iso-electronic principle, it is a well-known fact in valency theory that a group XH often has properties close to those of the " compound atom ". We therefore expect a similarity between the fluorine and hydrogen peroxide molecules. The fluorine molecule has a bond length of 1·45 A. and a bond energy at room temperature of 63·5 kcals. (Skinner, *loc. cit.*). The Raman spectrum of fluorine has not been measured and, in consequence, the force constant of the molecule is not known directly, but it may be estimated by extrapolating a graph of force constant against bond energy for the halogen molecules I_2, Br_2, Cl_2. Such a graph yields a value $3{\cdot}6 \times 10^5$ dynes/cm. for the fluorine force constant. The stretching force constant reported (Bailey and Gordon, *loc. cit.*) for the OO bond in hydrogen peroxide is also $3{\cdot}6 \times 10^5$ dynes/cm. [which value receives some confirmation since, *via* Badger's rule, it gives $r(\mathrm{OO})$ as 1·48 A., in good accord with the electron-diffraction value (Giguère and Schomaker, *J. Amer. Chem. Soc.*, 1943, **65**, 2025)]. Since k and r appear to be so closely similar

for the FF and $OO_{H_2O_2}$ bonds, we expect close similarity of E, in full agreement with our choice for $E(OO)_{H_2O_2}$.

Badger's rule (Garner and Yost, *J. Amer. Chem. Soc.*, 1937, **59**, 2738) yields a value 836 cm.$^{-1}$ for the fundamental frequency of F_2. This corresponds to $k \sim 4 \times 10^5$ dynes/cm. Gale and Monk (*Astrophys. J.*, 1924, **59**, 125; 1929, **69**, 77) have assigned the value 1130 cm.$^{-1}$ to this frequency. This corresponds to $k \sim 7{\cdot}1 \times 10^5$ dynes/cm. Gordy (*J. Chem. Physics*, 1946, **14**, 305), from an empirical relation involving bond length, has predicted $k(F_2)$ as $7{\cdot}93 \times 10^5$ dynes/cm. A value of this magnitude is obtained from a plot of force constant against bond length for I_2, Br_2, and Cl_2. The evidence against these high values includes: (*a*) they do not accord with Badger's rule; (*b*) Gordy's relation fails for the hydrogen molecule—it is not unlikely therefore that it fails also for the fluorine molecule; (*c*) they conflict with the similarity of iso-electronic molecules stressed here; (*d*) Gaydon ("Dissociation Energies," Chapman and Hall, 1947) has recently inclined to the view that $D(F_2)$ is rather less than 63·5 kcals.: while this may affect the argument of similarity between F_2 and H_2O_2, it certainly renders high values for $k(F_2)$ still less likely.

Continuing the sequence from F_2 to $(HO)_2$ to $(H_2N)_2$, we find the NN bond in hydrazine to have closely similar characteristics to the FF and peroxide bonds. It is known to have a bond length of 1·47 A. and a stretching force constant of $3{\cdot}6 \times 10^5$ dynes/cm. (Branch and Calvin, "Theory of Organic Chemistry", Prentice Hall, 1941). One may predict the NN bond energy in hydrazine to be close to 64 kcals., though the dissociation energy will probably be considerably lower, as it is in hydrogen peroxide. Table II shows the similarity between the $H_2N–NH_2$, HO–OH and F–F bonds. We should not expect the similarity to extend to the CC bond of ethane, since it is known that in ethane hybridisation of the 2*s* and 2*p* atomic wave functions becomes more important. The presence of *s* character in the carbon valencies makes the CC bond appreciably stronger than the NN, OO, or FF bonds (Walsh, in course of publication).

TABLE I.

Comparison of the halogens.

	k, 10^5 dynes/cm.	r, A.	E (room temp.), kcals./mole.		k, 10^5 dynes/cm.	r, A.	E (room temp.), kcals./mole.
I_2	1·72	2·667	36·4	Cl_2	3·29	1·989	58·1
Br_2	2·46	2·284	46·3	F_2	3·6 (est.)	1·45	63·5

TABLE II.

Comparison of N_2H_4, H_2O_2, *and* F_2.

	k, 10^5 dynes/cm.	r, A.	E, kcals./mole.
$H_2N–NH_2$	3·6	1·47	—
HO–OH	3·6	1·47	64
F–F	3·6 (est.)	1·45	64

There is thus a considerable body of concordant evidence against a value of 35 kcals. for $E(OO)_{H_2O_2}$ and in favour of $\sim$ 64 kcals. This must mean that the graph plotted by Glockler and Matlack, namely, of dissociation energy against r for different states of the O_2 molecule (built up from O atoms in different atomic states), is not a valid way of estimating the bond energy in hydrogen peroxide. It has to be emphasised in this connection that a smooth curve of E–r is only to be expected for bond energies as distinct from dissociation energies. These are not necessarily identical even for diatomic molecules. For example, as Mulliken (*J. Chem. Physics*, 1939, **7**, 28) has shown, the N→V character of the Schumann–Runge bands of O_2 and the ionic nature (in A.O. approximation) of the V state show that the $^3\Sigma_u^-$ state of O_2 must be considered as built, at least partly, from $O^{+}\,{}^4S + O^{-}\,{}^2P$—although the state dissociates into $O\,{}^3P + O\,{}^1D$. Penney ("Quantum Theory of Valency", Methuen, 1935) has described how the "valency state" of an atom in a molecule is not equivalent to its ground state; while Heitler ("Wave Mechanics", Oxford, 1945) has emphasised the interaction of potential energy curves as a result of the operation of the "non-crossing rule". It is clear that the dissociation energy of a molecule is not necessarily a quantity directly related to properties, such as force constant and inter-nuclear distance, characteristic of the equilbrium state of the molecule.

Finally, we may observe that the weakness of the OO bond (cf. the BH bond; Walsh, *J.*, 1947, 89) means that the orbital concerned in it has a large spatial spread. This is likely to prove a significant point in the understanding of peroxide chemistry; *e.g.*, it partly accounts for the formation of complexes in which the peroxide bond has attached to it an atom of acceptor properties such as a ferrous ion.

Bond Strengths in Other Peroxides.—The author has pointed out (*Trans. Faraday Soc.*, 1946, **42**, 264) that the variations in OO bond strength from molecule to molecule can partly be understood in terms of charge transfer effects established by the study of the ionisation potentials of non-bonding electrons in alkyl halides. The greater the negative charge transfer to the OO group, frequently the greater the OO bond strength. The OO strength should according to this view increase in the order H–OO–H, Me–OO–H, Et–OO–H, Pr^{β}–OO–H, Bu^{γ}–OO–H, while the corresponding dialkyl peroxides should be still more stable—though there may be offsetting factors, as discussed below. Milas and Surgenor (*J. Amer. Chem. Soc.*, 1946, **68**, 205) have confirmed the remarkable stability of di-*tert.*-butyl peroxide.* Berezovskaja, Varfolomeeva, and Stefanovskaja (*J. Physical Chem. Russia*, 1944, **18**, 321) have adopted a conclusion closely similar to ours, namely, that the stability of organic peroxides increases with the number of carbon atoms in the radicals attached to the OO group.

The trend of the peroxide bond strengths can be seen by considering the reaction

$$R{\cdot}O{\cdot}OR' \longrightarrow R{\cdot}OR' + O \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and using the heats of peroxide formation found by Stathis and Egerton (*Trans. Faraday Soc.*, 1940, **36**, 606). Assuming the CO and OH bonds and the internal bonds of the alkyl radicals to have the same strength in the peroxide as in the alcohol or ether, the heat absorbed by (1) readily gives the peroxide bond energy. For Et•O•OH, Pr•O•OH, and Et•O•OEt, the values come to 51, 54, and 62 kcals./mole, respectively. It is the trend only of these figures that is important. The absolute values must be low because, owing to polarity effects, (*a*) the CO bond will actually be weaker in R•O•OH than in R•OH, and (*b*) the OH bond will actually be weaker in R•O•OH than in R•OH—so that the energy absorbed by (1) is actually lower than E(OO). We therefore conclude that our value $\approx$ 64 kcals./mole for E(OO) in hydrogen peroxide is not inconsistent with the thermal data of Stathis and Egerton for the above three compounds and with the idea of increasing OO strength with increasing charge transfer.

According to the figure given by Kassatochkin (*Compt. rend. Acad. Sci. U.S.S.R.*, 1945, **47**, 193), from X-ray work, the bond length in the ion $^{-}O{-}O^{-}$ is only 1·35 A. as against 1·47 A. given by electron diffraction (Giguère and Schomaker, *loc. cit.*) (and by X-ray work in the case of the compound of urea with hydrogen peroxide; Lu, Hughes, and Giguère, *J. Amer. Chem. Soc.*, 1941, **63**, 1507) for the OO bond length in hydrogen peroxide; indicating a stronger bond in O_2^{--} than in hydrogen peroxide, in spite of the adjacent similar charges in O_2^{--}.

One may ask the reason for the increase of OO bond strength with increasing negative charge transfer to the bond. Up to a point, increasing the electronegativities of the atoms at the ends of a bond increases the bond strength [*e.g.*, $E(\mathrm{II}) < E(\mathrm{BrBr}) < E(\mathrm{ClCl}) < E(\mathrm{FF})$, and $E(\mathrm{SeSe}) < E(\mathrm{SS}) < E(\mathrm{OO})$ as shown above]; but it is clear that this increase of electronegativity as a means of increasing bond strength can go too far (cf. Walsh, *J. Chem. Physics*, 1947, **15**, 688): after a certain point it will weaken the bond because the atomic orbitals that have to overlap to give the bond become so small that strong overlap cannot occur because it would involve the nuclei being so close as to repel each other strongly. In such cases (which will only occur in bonds between atoms of high electronegativity) *decrease* of electronegativity of the bonded atoms will strengthen the bond. An example is the way the bond in F_2 strengthens if one of the F atoms is replaced by Cl to give FCl—in spite of the fact that the bond in FCl is polar. The peroxide bond apparently affords another example of this reduced overlap effect.

Rieche ("Alkylperoxyde und Ozonide," Steinkopf, Dresden, 1931, p. 128) suggests that the dipole moment of peroxides decreases in the sequence from hydrogen peroxide *via* alkyl hydroperoxides to dialkyl peroxides. Chromatographic analysis of peroxide mixtures (Eggersglüss, unpublished work) fully substantiates this. The greater dipole moment in alkyl hydroperoxides relative to dialkyl peroxides is one of the factors causing the former to have much higher boiling points than the latter. Thus the b. p. of $CH_3{\cdot}O{\cdot}OH$ is $\sim$ 40° at 65 mm., but that of $CH_3{\cdot}O{\cdot}OCH_3$ is only 13·5° at 740 mm., while that of *tert.*-butyl hydroperoxide is 33° at 17 mm., as against only 12—13° at 20 mm. for di-*tert.*-butyl peroxide. (Another, related, factor is of course the possibility of hydrogen bond formation in alkyl hydroperoxides.) At first sight this statement concerning the dipole moments appears to conflict with the statement that there is greater negative charge transfer to the OO group in a dialkyl than in an alkyl than in hydrogen

---

* Milas and Surgenor (*loc. cit.*, and *J. Amer. Chem. Soc.*, 1946, **68**, 643) and Milas and Perry (*ibid.*, p. 1938) have also confirmed the rules given by George and Walsh (*Trans. Faraday Soc.*, 1946, **42**, 94) for the decomposition of *tert.*-alkyl peroxides.

peroxide. Models of dialkyl peroxides, however, soon show that, whereas in hydrogen peroxide the angle between the planes containing the OH bonds is $\sim 100°$ (Penney and Sutherland, *Trans. Faraday Soc.*, 1934, **30**, 898; *J. Chem. Physics*, 1934, **2**, 492), the angle between the corresponding planes in dialkyl peroxides must be close to 180°. This is particularly so in di-*tert.*-butyl peroxide which must conform very closely to a *trans*-molecule. Hence, whereas in the hydrogen peroxide molecule the two OH dipoles only partly oppose each other, in dialkyl peroxides the corresponding dipoles must be in much greater opposition. Alkyl hydroperoxides, as a result of these steric effects, must occupy an intermediate position.

The reason for the skew nature of the hydrogen peroxide molecule is the repulsion of the charge clouds of the lone-pair electrons on the oxygen atoms: if these charge clouds were arranged with their axes parallel, the OO bond would be weakened, it is estimated, by some 10 kcals. (Penney and Sutherland, *loc. cit.*). In a peroxide such as di-*tert.*-butyl peroxide, therefore, it has to be remembered that, although the magnitude of the negative charge transfer to the OO group is a factor that probably tends strongly to increase the OO strength, on the other hand the *trans*-arrangement of the molecule will mean a weakening of OO strength by some 10 kcals. We may further observe that the smallness of the over-all dipole moment in di-*tert.*-butyl peroxide, relative to that of hydrogen peroxide, must be an important factor causing the chemical inertness of the molecule.

The above serves to emphasize that charge transfer can only be one of many factors affecting OO bond strengths. It should also be remembered that the partial correlation is with bond energies and not necessarily with *dissociation* energies. Further, although it can be shown that the reaction

$$CH_3{\cdot}CH_2{\cdot}O{\cdot}OH_{\text{vap.}} = CH_3 + H{\cdot}CHO + OH$$

absorbs 66·9 kcals. (Walsh, *Trans. Faraday Soc.*, 1947, **43**, 297), and though little or none of this energy is expected to be absorbed in the split

$$CH_3{\cdot}CH_2{\cdot}O = CH_3 + H{\cdot}CHO$$

[which breaks a CC bond (requiring $\gtrsim$ 80 kcals.: cf. Skinner, *Nature*, 1946, **158**, 592), forms a $>C{=}O$ from a $\neq C{-}O^-$ (evolving $\gtrsim 190 - 90$ kcals.: cf. Skinner, 1946, *loc. cit.*, with Walsh, *Trans. Faraday Soc.*, 1947, **43**, 60) and makes minor changes in CH strengths], the energy of activation of gas-phase peroxide decompositions lies near the range 30—40 kcals. (*e.g.*, Harris and Egerton, *Proc. Roy. Soc.*, 1938, *A*, **168**, 1). This means that the energy of activation apparently does not (as has sometimes been supposed) concern simply the fission of the OO bond and must be interpreted with great caution. In a probably similar way, nitrate and nitrite decompositions (Phillips, *Nature*, 1947, **160**, 753; Rice and Radowskas, *J. Amer. Chem. Soc.*, 1935, **57**, 350) have apparent activation energies near the range 30—40 kcals., although E(O–N) is probably considerably higher. [Thus, D(O–N) in HNO_3 can be shown to be $\sim$ 54 kcals.: cf. Skinner, 1945, *loc. cit.*] *

The Energy Evolved in the Reaction $H + O_2 = HO_2$.—A knowledge of the heat of the reaction

$$H + O_2 = HO_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

is essential for progress to be made in deciding the most probable reaction schemes governing the combustion of hydrogen and hydrocarbons.

Past estimates. Bodenstein and Schenk (*Z. physikal. Chem.*, 1933, *B*, **20**, 420), from a study of the inhibition by oxygen of the hydrogen–chlorine reaction, estimated the heat of reaction (2) to be about 40 kcals. Haber and Weiss (*Proc. Roy. Soc.*, 1934, *A*, **147**, 350), from consideration of the ferrous ion–hydrogen peroxide system, estimated a value $\sim$ 50 kcals. Bray (*J. Amer. Chem. Soc.*, 1938, **60**, 82) estimated 51 kcals. on the basis of several assumptions, including that of the ionisation constant of HO_2 being the same as that of HOCl. Others have used values varying between 40 and 50 kcals.

Bodenstein's estimate depends upon a particular set of reactions being assumed for the H_2–Cl_2–O_2 system. This set is by no means unique, and little reliance can be put upon the upper limit of 44 kcals. given by Bodenstein. Haber and Weiss's estimate depends upon several assumptions (*e.g.*, they assume a value for the experimentally unknown velocity constant of the reaction $Fe^{++} + HO_2 \longrightarrow Fe^{+++} + HO_2^-$). Also, their estimate, like that of Bray, is for

---

* The reduced overlap effect consequent upon too high an electro-negativity product should be less important for O–N than for O–O bonds. Also the high dipole of a NO_2 group causes a polarity in the ON bond of nitrates which is greater the greater the charge transfer from the alkyl groups to the O atom. For these and other reasons, it is not surprising that the order of stability to dissociation of ON bonds in alkyl nitrates is Me>Et>*n*-Pr(Phillips, *loc. cit.*).

reaction in solution. One can hardly conclude that the evidence for the energy evolved by (2) in the gas phase lying in the range 40—50 kcals. is at all strong. We propose in what follows to give several lines of evidence which suggest a value in the range 60—70 kcals.

Evidence from the electronic structure of O_2. Haber and Weiss (*loc. cit.*), estimating the energy of (2) to be 50 kcals., remarked " The great difference between this value and the much larger value for

$$H + HO_2 = H_2O_2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

is due to the fact that the double bond in the oxygen molecule must be opened to produce the first product, HO_2, but is already open for the second step to proceed ". This appears to be based upon an inadequate conception of the oxygen molecule. The paramagnetism of oxygen forces one to assume the existence of unpaired electrons in the molecule and therefore to abandon any close parallel between the bonding in the oxygen molecule and in the CC bond of ethylene. If we take an x axis along the OO bond, then one oxygen atom has a $2p_y$ odd electron and a $2p_z$ lone pair, while the other has a $2p_z$ odd electron and a $2p_y$ lone pair. Now the bonding that results from the interaction of an odd electron with an appropriate lone pair on an adjacent atom is considerable. For example, the first ionisation potential of a Cl_2 molecule corresponds to the removal of one of the non-bonding electons : that is, in Cl_2^+ one of the Cl atoms has an odd $2p_y$ electron, while the other has a $2p_y$ lone pair. Accordingly, we find the Cl–Cl bond to be appreciably stronger in Cl_2^+ than in Cl_2, as shown by the vibrational frequency and internuclear distance. This may in part be due to removal, in Cl_2^+, of some of the repulsion between two fully occupied p orbitals such as operates to make the hydrogen peroxide molecule skew, but the magnitude of the effect indicates an appreciable bonding due to the interaction of the odd $2p_y$ electron with the $2p_y$ lone pair.* Herzberg (1939, *op. cit.*) estimates $D(Cl_2^+)$ to be 4·4 v. (101 kcals.), while $D(Cl_2)$ is only 2·48 v. (57 kcals.). By analogy with the Penney–Sutherland treatment of hydrogen peroxide, the repulsion of two fully occupied p orbitals is hardly likely to account for much more than 10 kcals. of the difference. Pauling (" Nature of the Chemical Bond ", 1940) calls the interaction of an odd electron and a lone pair a " three electron bond " and finds evidence for such bonds being about half the strength of the corresponding normal electron-pair bonds. In this language the actual bond may be said to be a resonance hybrid of the two forms

$$\underset{(a.)}{\dot{A}\quad \ddot{B}} \qquad\qquad \underset{(b.)}{\ddot{A}\quad \dot{B}}$$

or the actual wave function of the system may be written neither as $\psi\ (a)$ nor as $\psi\ (b)$ but as $a\ \psi\ (a) + b\ \psi\ (b)$. In molecular orbital language, of the three electrons concerned, two go into a bonding orbital of form $A\ \psi\ (A) + B\ \psi\ (B)$ and one into an anti-bonding orbital of form $A\ \psi\ (A) - B\ \psi\ (B)$. This means a net bonding effect contributed by two electrons minus one electron, that is, a bonding roughly half that prevailing in a normal electron-pair bond—in agreement with Pauling's conclusion. In this sense the so-called " three-electron " bond might be called a " one-electron " bond.

The much greater strength of the OO bond in O_2 (118 kcals.) than in H_2O_2 (64 kcals. according to our estimate above) is to be attributed to the existence of two " three-electron " bonds in O_2. Each " three-electron " bond is about half the strength of an ordinary O–O single bond $[\frac{1}{2}(118 - 64) = 27]$—a deduction which appears to confirm the approximate correctness of our estimate of the OO strength in H_2O_2, though we shall consider the matter in more detail below.

The two " three-electron " bonds in the O_2 molecule lie in planes at right angles and, to a first approximation, breaking the first (by addition of H to give HO_2) might be supposed not to disturb the second. Since the reaction

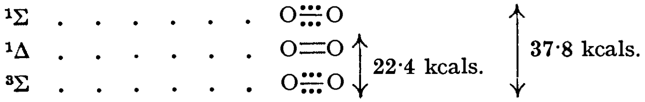
$$H + O_2 + H = H{\cdot}O{\cdot}OH \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

is known to liberate 138 kcals. (see the heat of atomisation of hydrogen peroxide quoted above), we might expect (2) to liberate 69 kcals. This figure has indeed been used by earlier authors (*e.g.*, Frankenburger and Klinkhardt, *Trans. Faraday Soc.*, 1931, **27**, 431; Dawsey, Urey, and Rice, *J. Amer. Chem. Soc.*, 1929, **51**, 1371), but the separation of (4) into two thermally equal steps has not previously been justified. We have, however, neglected certain points which it is necessary to consider in order to give the best estimate for the heat evolved by (2).

---

* In molecular-obitatal language, of course, the greater strength of Cl_2^+ than of Cl_2 is due to the removal of an electron from an anti-bonding orbital.

In the first place we have neglected the stabilising interaction of the two " three-electron " bonds in the oxygen molecule (Wheland, *Trans. Faraday Soc.*, 1937, **33**, 1499). Pauling (*op. cit.*, p. 253) gives the low-lying electronic states of the oxygen molecule as



The interaction of the two " three-electron " bonds may be either stabilising or repulsive : the $^1\Sigma$ state corresponds to the latter and the $^3\Sigma$ (or ground) state to the former. From the difference in the energies of the $^1\Sigma$ and $^3\Sigma$ states, the stabilising interaction of the two " three-electron " bonds in the ground state may be given as 18·9 kcals. The energy of the σ bond is expected to be not far from its value in hydrogen peroxide (cf. the usually assumed rough constancy of σ CC bonds) : in both O_2 and H_2O_2 the charge clouds of the lone-pair electrons are oriented so as not to cause repulsion. Since the ground-state bond energy is 118 kcals., we may therefore estimate the energy of each " three-electron " bond as $\sim \frac{1}{2}(118 - 19 - 64) = 17·5$ kcals. In the second place, the molecular-orbital description of the " three-electron " bond shows clearly that in this case it is not so much the σ bond that should be twice the strength of the " three-electron " bond, but a π bond between the nuclei In the $^1\Delta$ state there are no unpaired electrons and the bonding is somewhat analogous to that in ethylene. In this state, the bond energy is $118 - 22·4$ kcals. Hence the energy of the second (or π) bond in this state must be about $118 - 22 - 64 = 32$ kcals., and we note that the energy of each " three-electron " bond *is* roughly half this.

As compared with water, the two OH bonds in H_2O_2 are separated by an extra atom and also lie in different planes : removal of one H from H_2O_2 (unlike the case with H_2O) will leave the other OH bond almost unchanged ; that is, $E(OH)_{H_2O_2} = E(OH)_{HO_2}$ to a good approximation. On passing from $O\overset{\cdots}{\underset{\cdots}{-}}O$ $^3\Sigma$ to $\underset{H}{}\diagup O\overset{\cdots}{-}O$, we break a "three-electron" bond ($\sim$ 17·5 kcals.), remove the stabilising interaction of the two " three-electron " bonds ($\sim$ 19 kcals.), and liberate an energy in forming the OH bond that must be close to that of $E(OH)_{H_2O_2}$ (*i.e.*, 96 kcals.). The net liberation of heat is thus $96 - (17·5 + 19) \simeq 60$ kcals.

It is true that this calculation still neglects certain subsidiary effects—such as the change in strength of the second " three-electron " bond consequent upon the slight moving apart of the nuclei on breaking the first " three-electron " bond ; the change in strength of the σ bond from HOOH to HO_2 to O_2 ; and the effect of the polarity of the OH bond in HO_2 on the OO strength (cf. the change in OO strength with charge transfer discussed earlier) but, in view of the uncertainty of the figures, the agreement with the figure required by other lines of evidence (see below) is not unsatisfactory. It is, however, just worth considering what effect on the result would come from taking a different value for the OO strength in H_2O_2. Using a figure lower by x for $E(OO)_{H_2O_2}$, we obtain $17·5 + x/2$ for the energy of each " three-electron " bond and $96 + x/2$ for the energy of the OH bond in H_2O_2, so that the calculation of heat liberation is actually independent of x. On the other hand, as x increases, the strength of the " three-electron " bond becomes appreciably more than half that of the π bond in the $^1\Delta$ state.

It is also worth considering what would be the effect on the result if the energies of bonds involving O atoms were taken as related to a " valency state " of O y kcals. above the ground state. The high value of the O_2 force constant as compared with those of other bonds of known energy affords some justification for taking $E(O_2)$ as greater than $D(O_2)$, in order to preserve the utility of the concept of bond energy as a parameter related to bond force constants, irrespective of the nuclei concerned. Similarly, the force constants of OH bonds indicate bond energies greater than those obtained from heats of atomisation relating to oxygen atoms in the ^3P state. $E(O_2)$ then becomes $118 + 2y$ kcals. and $E(OH)_{H_2O_2}$ becomes $96 + y$ kcals. Hence $E(OO)_{H_2O_2}$ remains at 64 kcals. The energy of the " three-electron " bond in O_2 becomes $17·5 + y$ kcals. Therefore, the energy evolved by (2) becomes $96 + y - (17·5 + y + 19)$; *i.e.*, it remains unchanged at $\sim$ 60 kcals.

Taking $E(OH)_{HO_2}$ as 96 means that an estimate of 45 kcals. for the energy liberated by (2) implies an OO bond strength in HO_2 of only 67 kcals. This is hardly compatible with the magnitude of the interaction that we expect to occur between the $2p_z$ odd electron and the $2p_z$ lone pair. An estimate of 60 kcals. for the energy liberated by (2) corresponds to an OO bond strength in HO_2 of 82 kcals./mole. It further corresponds to an energy liberated in (3) of 78 kcals.

So far, we have spoken mainly in terms of atomic orbital or pair-bond theory. On the molecular orbital theory, the oxygen molecule possesses (only orbitals built from $2p$ atomic orbitals being considered) six electrons in bonding orbitals and one electron in each of two anti-bonding orbitals. On passing from O_2 to HO_2, the OO strength weakens because the extra electron provided by the H atom passes partly into one of the OO anti-bonding orbitals. The structure approaches that obtained by fusing the H and one of the O nuclei, namely FO. The effect, in terms of energy, of an anti-bonding electron in O_2 is roughly given by $E(O_2^+) - E(O_2)$, *i.e.*, by $6{\cdot}48 - 5{\cdot}08$ v. $= 1{\cdot}40$ v. $= 32$ kcals. Hence, if formation of O–H liberates ~ 96 kcals., the energy evolved by (2) $= 64$ kcals. This is likely to be a minimum value since two of the OO anti-bonding electrons in HO_2 are now spending part of their time, not in the OO, but in the OH bond.

Evidence from interatomic distances of O_2, O_2^-, *and* O_2^{--}. Kassatochkin (*loc. cit.*) lists the following interatomic distances based on X-ray work :

O_2 1·20 A. O_2^- 1·27 A. O_2^{--} 1·35 A.

These distances support the thesis that the OO bond weakens roughly as much in going from O_2 to O_2^- as from O_2^- to O_2^{--}; and therefore by implication that, to a first, crude, approximation, destruction of one " three-electron " bond in the oxygen molecule leaves the other unaffected. Kassatochkin calculates $D(O_2^-)$ as 3·82 v. (88 kcals.), although the result is somewhat uncertain since it depends upon a value for the electron affinity of an oxygen atom (which he takes as 2·2 v. or 51 kcals.) and assumes the lattice energies of KCl and KO_2 to be the same. It is of interest, however, to note that his result, compared with $D(O_2) = 5{\cdot}09$ v., means a decrease in OO strength of 1·27 v. or 29 kcals./mole, in good agreement with our figure of 32 kcals. above, in passing from O_2 to O_2^-. The extra repulsion of parallel lone-pair charge clouds that must occur in O_2^- being neglected, (2) should liberate $96 - 29 = 67$ kcals. Inclusion of the charge-cloud repulsion will raise this estimate, but not by much, since, in any case, owing to the polarity of the OH bond in HO_2, the condition of the OO group in HO_2 cannot be very different from that in the O_2^- ion. A value for the electron affinity of an oxygen atom higher by x kcals. would reduce the calculated energy in (2) by x.

Kinetic evidence from the H_2–O_2–NO_2 *system.* The kinetics of the thermal and photochemical H_2–O_2–NO_2 systems at temperatures above 300° are so similar that there can be little doubt that the NO_2 acts in the same way in both systems (Norrish and Griffiths, *Proc. Roy. Soc.*, 1933, *A*, **139**, 147). Since in the photochemical system NO_2 is known to act by decomposition to NO + O, the conclusion is that in the thermal system NO_2 is also dissociated to NO + O. This decomposition requires 71·5 kcals./mole (Gaydon, 1947, *loc. cit.*; the value 73 kcals. results from figures given by Biochwsky and Rossini, " Thermochemistry ", Reinhold, 1936). Dainton and Norrish (*Proc. Roy. Soc.*, 1941, *A*, **177**, 393) found evidence that NO_2 molecules were dissociated on collision with energy-rich links in the oxidation chains. The only plausible suggestion as to the nature of the " hot " links is—as Dainton and Norrish supposed—that they are HO_2 molecules carrying their energy of formation from H + O_2. Since an activation energy of 15 kcals. was found for the reaction whereby NO_2 is dissociated, we must have

$$15 + \text{energy evolved in (2)} \geqq 71{\cdot}5$$

or

$$\text{energy evolved in (2)} \geqq 56{\cdot}5 \text{ kcals.}$$

Evidence from HBr–O_2 *systems.* The sensitisation by O_2 of HBr additions to olefins at room temperature and of hydrocarbon oxidation by HBr [Vaughan and Rust, U.S.PP. (1946) 2,395,523; 2,403,722; 2,403,771] at temperatures around 150° is probably due to the formation of Br atoms by the reaction

$$HBr + O_2 = HO_2 + Br$$

Now $D(HBr) = 83$ kcals./mole (Herzberg, 1939, *loc. cit.*). Hence if (2) only liberates 45 kcals., an energy of activation (E_A) of at least 38 kcals. is needed. A reaction with such an E_A is not likely to be appreciable at temperatures as low as those at which the above-mentioned sensitisations occur. If, however, (2) liberates, say, 60 kcals., an E_A of only 23 or more is needed, which is more plausible for the observed temperature range of reaction.

[Since $D(HCl) = 103$ kcals. (Herzberg, 1939, *loc. cit.*), hydrogen chloride is only likely to bring about similar sensitisation at high temperatures. Norrish and Foord (*Proc. Roy. Soc.*, 1936, *A*, **157**, 503) find that it sensitises the oxidation of methane in the temperature range 600—700°.]

Conclusion.—Although it is not at present possible to arrive at a precise estimate of the energy evolved in the gas phase by the reaction $H + O_2 = HO_2$, the cumulative effect of the above lines of evidence is to suggest that past estimates in the range 40—50 kcals. are too low. Until more precise evidence is forthcoming, it seems more accurate to take a value in the range 60—70 kcals. While this change may not seem very great, it is in fact of considerable significance for the reaction schemes postulated to represent the combustion of hydrogen and hydrocarbons.

HO_2 is inert for much the same reason as the O_2 molecule (in spite of its containing two unpaired electrons) is inert compared with many atoms or radicals : its odd electron is concerned in an attractive interaction with a parallel lone pair. Its inertness is shown, for example, in the inhibition by O_2 of the H_2–Cl_2 reaction and is reflected in the large energy evolved by reaction (2). In the same way the isoelectronic Cl_2^+ molecule has a high bond strength.

We conclude by considering very briefly the relevance of our discussion of the " three-electron " bonds in the oxygen molecule to the formation of organic peroxides from hydrocarbons.

Formation of Organic Peroxides from Hydrocarbons.—There is at present (see Symposium on Oxidation, *Trans. Faraday Soc.*, 1946, **42**, 99—398) unanimity of opinion that organic peroxides are formed from hydrocarbons during oxidation by the chains

$$R + O_2 = R{\cdot}O{\cdot}O \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

$$R{\cdot}O{\cdot}O + RH = R{\cdot}O{\cdot}OH + R \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

where R is a hydrocarbon radical. There has been, however, only one careful consideration of the thermochemistry of these reactions, namely, that by Bolland and Gee (*Trans. Faraday Soc.*, 1946, **42**, 244). The energy liberated by (5) is mainly given by the expression

Energy liberated in forming R–O	—	Energy absorbed in breaking a three-electron bond	—	Energy of interaction of two three-electron bonds	—	Resonance energy of radical R
(*X*)		(*Y*)		(*Z*)		(*R*)

X will be slightly less than its value in methyl alcohol (90 kcals. : Skinner, *Nature*, 1946, **158**, 592) since the bond is expected to be more polar and therefore slightly weaker in a peroxide radical : a rough value might be 85 kcals. as a minimum. The energy liberated is therefore $\approx 85 - (17{\cdot}5 + 19) - R$ or $48 - R$ kcals.

Reaction (6) liberates the energy of an OH bond (~ 98 : slightly greater than in H_2O_2 because of charge transfer from R to the OO group) plus the resonance energy of the hydrocarbon radical formed (R) minus the energy of a CH bond (~ 100 kcals.) minus the energy of a three-electron bond ($\sim 17{\cdot}5$). Hence the energy liberated is $\approx 98 - 100 - 17{\cdot}5 + R$ or $\approx R - 19{\cdot}5$ kcals. Bolland and Gee arbitrarily took 15 instead of 17·5 kcals., and since they used the value of the OH strength in water (110 kcals.) they calculated a greater exothermicity than here; (5) will be a strongly exothermic reaction. In olefinic systems [where also $E(CH)_{\alpha\text{-methylene}}$ may be less than 100], R may be sufficiently large (Bolland and Gee, *loc. cit.*) that (6) is also nearly, if not quite, exothermic. In paraffinic systems, however, R is probably small, so that it is difficult to escape the conclusion that (6) must be endothermic. It becomes necessary to suppose that if (6) occurs it does so with an activation energy, or else that the peroxide radical formed in (5) carries with it into (6) some of its energy of formation (it will certainly carry vibrational energy, since the OO distance increases when RO_2 is formed from O_2). In the latter case, much of the energy of peroxide decomposition may also be provided, thus accounting for the small yields of peroxides actually found.

Bolland (*Proc. Roy. Soc.*, 1946, *A*, **186**, 218) finds the energy of activation of (6) (where RH is ethyl linoleate) to be significantly in excess of that for (5), in agreement with the present discussion.

I am indebted to Dr. L. H. Long for stimulating discussion, and to Imperial Chemical Industries for the gift of a set of polythene atomic models.

LABORATORY OF PHYSICAL CHEMISTRY, CAMBRIDGE. [*Received, February 27th,* 1947.]