168. *Pernitrous Acid. The Reaction between Hydrogen Peroxide and Nitrous Acid, and the Properties of an Intermediate Product.*

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The rate of the reaction between hydrogen peroxide and nitrous acid, at low acidities, is shown to be proportional to the concentrations of hydrogen peroxide, nitrous acid, and hydrogen ion. This reaction, and the reactions of nitric oxide and nitrogen dioxide with hydrogen peroxide, are shown to produce pernitrous acid. A product of all the reactions, believed to be the pernitrous acid, initiates the polymerisation of methyl acrylate and also hydroxylates and nitrates benzene. To explain these observations a free-radical mechanism is proposed in which it is suggested that pernitrous acid undergoes homolytic fission to give hydroxyl radicals and nitrogen dioxide.

Despite a considerable literature, the nature and, in a measure, the properties of the peroxy-compounds of nitrogen remained uncertain. Of the two per-acids more definitely postulated, the more clearly defined was pernitrous acid; the other, pernitric acid, has been described as resulting from admixture of concentrated hydrogen peroxide and nitrogen pentoxide (Schwarz, *Z. anorg. Chem.*, 1948, **256**, 1) or by bombardment of nitric acid with fast electrons (Allen, *J. Phys. Coll. Chem.*, 1948, **52**, 479). The deduction that it is HNO_4, admittedly reasonable, does not appear to be supported by quantitative evidence. Earlier writers did not distinguish between the per-compounds; and many observations, attributed to reactions of pernitric, actually refer to pernitrous acid.

From the interaction of alkyl nitrites and ethyl hydroperoxide, Baeyer and Villiger (*Ber.*, 1901, **34**, 755) inferred that the reaction between hydrogen peroxide and nitrous acid involved the formation of an unstable pernitrous acid. In 1904, Raschig (*Z. angew. Chem.*, 1904, **17**, 1419; *Ber.*, 1907, **40**, 4585) showed that a mixture of hydrogen peroxide and nitrous acid is a stronger oxidising agent than either of its components but ascribed the fact to the presence of pernitric acid, formulated as HNO_4. However, the oxidising properties of the mixture led Schmidlin and Massini (*Ber.*, 1910, **43**, 1170) to call the new substance a hydroperoxide of nitrous acid, HO·ONO, not pernitric acid. Trifonow (*Z. anorg. Chem.*, 1922, **124**, 123, 136) and Pollak (*ibid.*, 1925, **143**, 143) attempted to establish the formula of the per-acid by observing the hydrogen peroxide : nitrous acid ratio which gave the maximum liberation of bromine from hydrobromic acid. Pollak found no recognisable stoicheiometric relation between the reactants but Trifonow's measurements led him to call the initial product dinitryl peroxide, N_2O_6, which he believed was rapidly hydrolysed by water to pernitric acid. In this paper, Trifonow mentioned the transient yellow colour assumed by the mixture (in the absence of hydrobromic acid) : this he attributed to the release of nitrogen dioxide in the solution.

In 1929, Gleu and Roell (*ibid.*, **179**, 233) showed that the oxidation of aqueous sodium azide by ozone produced a relatively persistent yellow colour and described it as due to sodium pernitrite. This they were unable to isolate, but, from an analysis of the solution, they formulated it as $NaNO_2O$. Six years later Gleu and Hubold (*ibid.*, **223**, 305) concluded from the analysis of a similar yellow solution, prepared by mixing acidified hydrogen peroxide with sodium nitrite and immediately making the whole alkaline with sodium hydroxide, that they were dealing with the same compound. Kortum and Finckh (*Z. physikal. Chem.*, 1941, *B*, **48**, 32), showed that the yellow solutions had an ultra-violet absorption band with a maximum close to that of the nitrate ion, but about fifteen times more intense and much broader.

In face of the above evidence, and after many of the conclusions described in this communication had been reached, Abel (*Monatsh.*, 1949, **80**, 449) denied the existence of pernitrous acid and ascribed the colour observed in acid solution to nitrogen dioxide. He criticised the formula, $HNO_2{\cdot}O$, on the grounds that Gleu and Hubold's experimental results indicate a ratio of one gram-equivalent (not one gram-atom) of active oxygen to one mole of nitrous acid, which would correspond to $(HNO_2)_2O$. It appears to us that Abel's criticism may have arisen from the fact that Gleu and Hubold used the oxidation–reduction equivalent of nitrous acid, *i.e.*, one-half of the molecular weight, when tabulating their results. If this is taken into consideration their deduction is correct and, furthermore, is substantiated by Rius and Foz (*Anal. Fís Quím.*, 1940, **36**, 308) whose analysis of the yellow solution by a potentiometric method gave identical results.

The present work aimed at securing further information about the reaction between hydrogen peroxide and nitrous acid. It has been possible to examine some of its kinetic features in solutions of very low acidity over a limited concentration range. The general rate expression obtained does not appear to correspond with that in a paper (which we have only seen in abstract) by Schilow, Rybakow, and Pal (*Bull. Inst. Polytechn. Ivanovo-Vosniesinsk*, 1930, **15**, 85; *Chem. Zentr.*, 1931, II, 377). The frequently contradictory previous evidence has led us to repeat some of the earlier work. The formation of the unstable yellow intermediate in the reaction in acid solution was at once confirmed, and by devising a flow method using alternately a tube and a channel its properties have been more precisely observed. In particular it has been unequivocally shown to be the precursor of the very much more stable yellow alkaline solution which Gleu and his co-workers claimed to contain sodium pernitrite, NaO•ONO. This claim being admitted, the yellow unstable intermediate would appear to be pernitrous acid, HO•ONO.

Experiments are now described which appear to invalidate the arguments of those who have sought to establish the formula of the per-acid by observing the liberation of bromine from hydrobromic acid. We have found that the short lived pernitrous acid appears in the oxidation, severally, of nitric oxide and nitrogen dioxide with hydrogen peroxide: both reactions seem to involve, as a preliminary step, the formation of nitrous acid.

Our polymerisation experiments show that mixing acidified hydrogen peroxide and a nitrite produces free radicals. But the acidification of sodium pernitrite has also been shown to cause the polymerisation of methyl acrylate; whence we argue that the free radicals are not produced during the formation of the pernitrous acid, but appear in the course of its decomposition.

Trifonow (*loc. cit.*) had previously observed that, if benzene is present when pernitrous acid is formed, both benzene and the aqueous solution become yellow, which, owing to a darkening induced by alkali, he ascribed to the formation of phenols. We have now isolated these phenols and relate their presence and the polymerisation of methyl acrylate to the liberation of hydroxyl radicals. In addition to the phenols formed from benzene in these circumstances, we find, remarkably, an appreciable amount of nitrobenzene. This new process of nitration applicable to hydrocarbons and other compounds is of especial interest in that it takes place at the ordinary temperature and in an aqueous media of low acidity. Its investigation is described by the authors in the succeeding paper.

EXPERIMENTAL

Kinetic features of the reaction between hydrogen peroxide and nitrites.

Under neutral conditions hydrogen peroxide and sodium nitrite do not react, but on acidification with a mineral acid reaction is immediate and extremely fast. Indeed, acidified hydrogen peroxide can be titrated with sodium nitrite solution, titanium sulphate being used as an internal indicator responding to hydrogen peroxide. When 1% sodium nitrite is added to dilute acidified hydrogen peroxide, the indicator becomes colourless when the molecular ratio $NaNO_2 : H_2O_2$ equals 1 : 1·05. Should, however, hydrogen peroxide be added to acidified sodium nitrite, the indicator develops colour when the ratio of 1 : 0·99 is reached, the smaller peroxide requirement being probably due to loss of nitrous acid. These results suggest the, presumably rapid, reaction

$$H_2O_2 + HNO_2 \longrightarrow HNO_3 + H_2O \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

We found that, when excess of hydrogen peroxide was used and back-titrated with potassium permanganate, the ratio nitrite : peroxide depended on addition of the hydrogen peroxide; when addition is dropwise, the ratio is 1 : 0·96, but when very rapid 1 : 0·85.

On changing from excess of mineral acid to a concentration giving a pH of *ca.* 4, we got measurable reaction rates. These were ascertained by decomposing the residual hydrogen peroxide, after known intervals, with manganese dioxide, and measuring the oxygen evolved, in a gas burette. Fairly consistent results were obtained, and, as a useful check, when the reaction was allowed to run its full course, the ratio proved to be 1 : 1, in conformation with equation (1). Measurements were made in solutions containing 5 c.c. of 0·2M-sodium nitrite, 10 c.c. of 1% hydrogen peroxide and, respectively, 5·5, 5·0, 4·5, and 4·0 c.c. of 0·0109N-

FIG. 1.

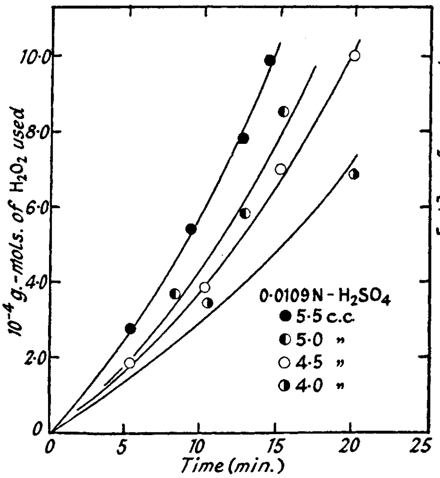


FIG. 2.

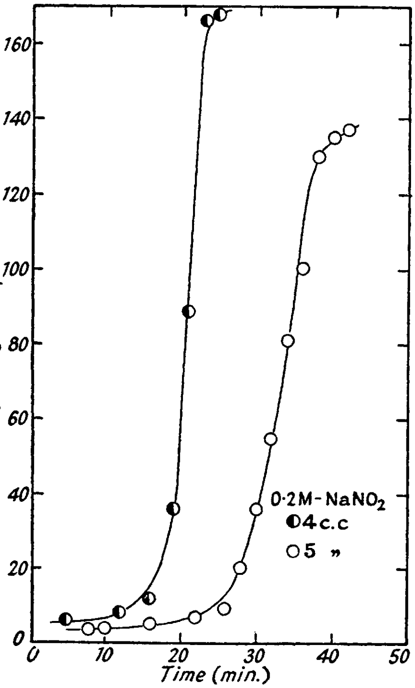


FIG. 3.

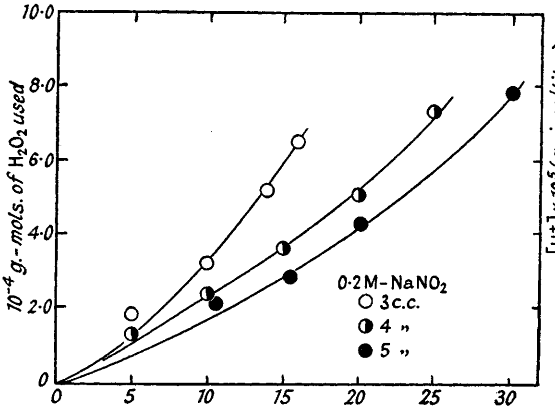
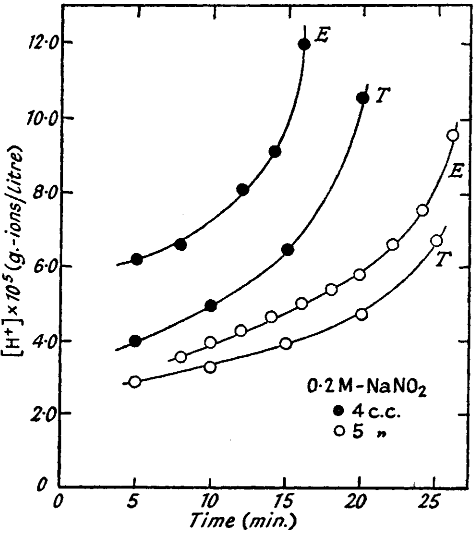


FIG. 4.



T, Calc. *E, Exptl.*

sulphuric acid in a total volume of 35 c.c. The amounts of hydrogen peroxide used are expressed graphically in Fig. 1.

The rate of consumption of hydrogen peroxide increased rapidly with time, which is understandable if hydrogen-ion concentration governs the speed, since the pH decreases in the course of the reaction. This is because, the added mineral acid being insufficient to convert all the nitrite into nitrous acid, the hydrogen-ion concentration is due entirely to the dissociation of nitrous acid, which is itself reduced by the common-ion effect of the excess of nitrite; but, as the reaction proceeds, the excess of nitrite is oxidised to nitrate with a consequential increase in hydrogen-ion concentration through reduction in the common-ion effect. Measurements of pH with a glass electrode during the reactions of solutions containing 5 c.c. of 0·0109N-sulphuric acid, 5 c.c. of 0·36M-hydrogen peroxide, 4 and 5 c.c. of 0·2M-sodium nitrite, in a total volume of 35 c.c., plotted against time in Fig. 2, show that the hydrogen-ion concentration actually does increase rapidly in the course of the reaction.

Rates of reaction in these two systems, and in another containing 3 c.c. of 0·2M-sodium nitrite, are plotted in Fig. 3. The rate is greater in solutions with less nitrite, probably because the reactant is nitrous acid; the nitrite ion as such reduces the rate by lowering the hydrogen-ion concentration.

From the rate curves for 4 and 5 c.c. of nitrite (Fig. 3) the hydrogen-ion concentration after certain times can be calculated, on the assumption that it is due to nitrous acid the dissociation of which is influenced by nitrite ion. These for the early stages of the reaction are plotted, along with the experimentally measured values, in Fig. 4. The calculated values are lower than the observed, possibly because the value of K_a available was for 12·5° and the actual temperature was 19°; but they are sufficiently close to support the view advanced. The difference in the initial rates, evident in Fig. 3, must be due to differences in initial concentrations of nitrite ion and/or of hydrogen ion since the initial concentration of hydrogen peroxide was constant and that of nitrous acid almost constant.

$$\begin{aligned}
\text{Let initial rate} &= K \times [\mathrm{H^+}]^x[\mathrm{NO_2^-}]^y \\
\text{Since}\quad [\mathrm{H^+}] &= K_a[\mathrm{HNO_2}]/[\mathrm{NO_2^-}] \\
[\mathrm{NO_2^-}] &= K'/[\mathrm{H^+}] \\
\text{Therefore, initial rate} &= K''[\mathrm{H^+}]^x/[\mathrm{H^+}]^y = K''[\mathrm{H^+}]^{x-y}
\end{aligned}$$

The initial rates, obtained from Fig. 3, when plotted against the calculated hydrogen-ion concentration, exhibit a straight line passing through the origin (equation : initial rate $=$ 0·615[H⁺]) (see Table 1) and indicate an initial rate directly proportional to the hydrogen-ion concentration, *i.e.*, $x - y = 1$. In Fig. 1 (H_2O_2 constant) the concentrations of nitrous acid approximate to those of sulphuric acid, and the concentrations of nitrite to the difference between the initial nitrite and the sulphuric acid (*i.e.*, a — H_2SO_4 concn., where a equals initial $NaNO_2$ concn.).

TABLE 1.

0·2M-$NaNO_2$ (c.c.)	10^5[H⁺] calc. (M)	$10^5 \times$ Initial rate (g.-mol. H_2O_2/min.) (N)	N/M (observed)
3·0	4·6	2·85	0·620
4·0	3·35	2·1	0·627
5·0	2·65	1·6	0·604

(N/M, determined from graph, = 0·615.)

$$\begin{aligned}
\text{Let initial rate} &= K[\mathrm{H^+}]^x[\mathrm{NO_2^-}]^y[\mathrm{HNO_2}]^z \\
&= K'[\mathrm{H^+}]^{x-y}[\mathrm{HNO_2}]^{z+y}
\end{aligned}$$

Initial rates, calculated hydrogen-ion concentrations, and nitrous acid concentrations (derived from Fig. 1) are given in Table 2. The initial rate, when plotted against $[\mathrm{H^+}][\mathrm{HNO_2}]$, gives a straight line passing through the origin {equation : initial rate/$([\mathrm{H^+}][\mathrm{HNO_2}])$ = 9·4}. Hence, the initial rate $= K[\mathrm{H^+}][\mathrm{HNO_2}]$ and both $(x - y)$ and $(z + y)$ have the value of unity, whence either $x = 1$, $y = 0$, $z = 1$; or $x = 2$, $y = 1$ and $z = 0$, *i.e.*, (*a*) initial rate $= K[\mathrm{H^+}][\mathrm{HNO_2}]$, or (*b*) initial rate $= K'[\mathrm{H^+}]^2[\mathrm{NO_2^-}]$. Owing to the interdependence of $[\mathrm{H^+}]$ and $[\mathrm{NO_2^-}]$, nitrite cannot be conclusively ruled out as a reactant. But there is no evidence that

TABLE 2.

$0{\cdot}0109$N-H_2SO_4 (c.c.)	$10^5[H^+]$, calc. (g.-ions/l.)	$10^3[HNO_2]$ (g.-mol./l.)	$10^8[H^+][HNO_2]$ (A)	10^6 Initial rate (g.-mol. H_2O_2/min.) (B)	$10^{-2}B/A$ (observed)
5·5	2·93	1·71	5·01	4·8	9·6
5·0	2·65	1·55	4·10	3·8	9·3
4·5	2·36	1·4	3·31	3·0	9·0
4·0	2·1	1·25	2·63	2·6	9·9

($10^{-2}B/A$, determined from graph, = 9·4.)

the nitrite ion reacts as such, and, since the adoption of (*b*) requires the implausible exclusion of $[HNO_2]$ as a rate-determining factor, equation (*a*) which implies that the rate varies directly with both nitrous acid and hydrogen ion is chosen.

FIG. 5.

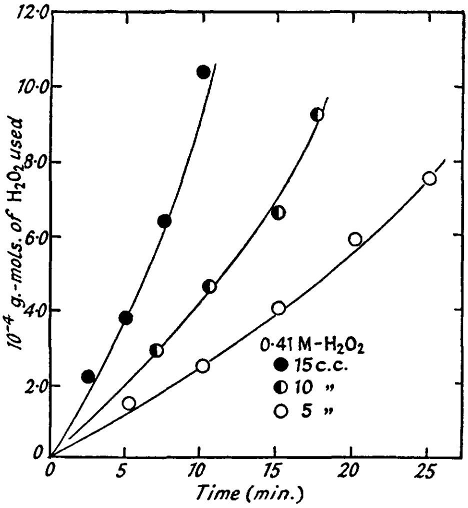
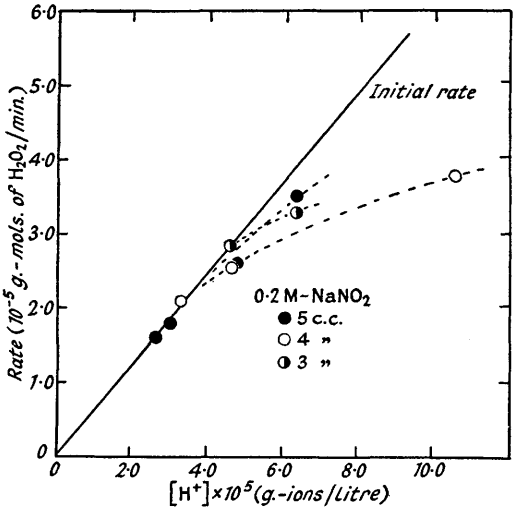


FIG. 6.



The effect of hydrogen peroxide on the reaction rate, shown in Fig. 5, was observed by measuring the amount of available oxygen used after various times in solutions (total volume, 35 c.c.) containing nitrite (5 c.c.; 0·2M.), sulphuric acid (5 c.c.; 0·0109N.) and, severally, 15, 10, and 5 c.c. of hydrogen peroxide (1%). The initial rates (Fig. 5) and the corresponding initial hydrogen peroxide concentrations give a straight-line plot passing through the origin (equation : initial rate/$[H_2O_2]$ = $0{\cdot}354 \times 10^{-3}$) (Table 3) and show that the rate is directly proportional to the concentration of hydrogen peroxide.

TABLE 3.

$0{\cdot}41$M-H_2O_2 (c.c.)	$[H_2O_2]$ (g.-mol./l.) (C)	$10^4 \times$ Initial rate (g.-mol. H_2O_2/min.) (D)	$10^3D/C$ (observed)
15	0·176	0·64	0·363
10	0·117	0·40	0·343
5	0·059	0·22	0·373

($10^3D/C$, determined from graph, = 0·354.)

The foregoing results which deal only with the initial stages of the reaction lead to the following rate equation

$$R = -d(H_2O_2)/dt = K[H_2O_2][HNO_2][H^+]$$

Values for K have been calculated using the initial rate (R) and other data :

(i) $R/[H^+] = K[H_2O_2][HNO_2]$
$R/[H^+] = 6{\cdot}15 \times 10^{-1}$ (Table 1); $[H_2O_2] = 5{\cdot}1 \times 10^{-2}$; $[HNO_2] = 1{\cdot}56 \times 10^{-3}$ (Fig. 3)

whence $K = 7{\cdot}73 \times 10^3$.

(ii) $R/[H_2O_2] = K[H^+][HNO_2]$
$R/[H_2O_2] = 3{\cdot}54 \times 10^{-4}$ (Table 3); $[H^+] = 2{\cdot}66 \times 10^{-5}$; $[HNO_2] = 1{\cdot}56 \times 10^{-3}$ (Fig. 5)

whence $K = 8{\cdot}57 \times 10^3$.

(iii) $R/([HNO_2][H^+]) = K[H_2O_2]$
$R/([HNO_2][H^+]) = 9{\cdot}42 \times 10^2$ (Table 2); $[H_2O_2] = 1{\cdot}06 \times 10^{-1}$ (Fig. 1)

whence $K = 8{\cdot}9 \times 10^3$.

Thus, K (mean) $8{\cdot}4 \times 10^3$ (concn., g.-mol.; time, minutes).

Some of the increase in rate during the reaction is derived from the change in hydrogen-ion concentration. That it comes mainly from this, and little if at all from chain propagation through an intermediate compound, is made evident by plotting (Fig. 6) calculated hydrogen-ion concentrations against measured rates, the former being deduced by the hydrogen peroxide remaining at a given instant and the latter by drawing tangents to the curves in Fig. 3. In all cases the observed rate is less than the rate calculated from the hydrogen-ion concentration (if changes in the concentrations of the other reactants are ignored).

The validity of the rate equation with $K = 8{\cdot}4 \times 10^3$ (see above) has been tested over the limited range studied. Arbitrary points taken on curves in Figs. 1, 3, and 5 have provided values to introduce into the rate equation. Rates so obtained, and the experimental rates derived from the selected points on the curves, may be compared in Table 4 in which they show an agreement, in spite of the approximations involved in arriving at the calculated rate, which augurs well for the correctness of the equation in expressing the course of the reaction within the limited concentration ranges of the reactants, *viz.*, $[H^+]$ 2—4·6 × 10^{-5} g.-ions per l., $[HNO_2]$ 1·2—1·7 × 10^{-3} g.-mol. per l., $[H_2O_2]$ 0·6—1·8 × 10^{-1} g.-mol. per l.

TABLE 4.

Points selected	$10^5[H^+]$ (g.-ion/l.)	$10^3[HNO_2]$ (g.-mol./l.)	$10^2[H_2O_2]$ (g.-mol./l.)	10^5 × Rate, calc. (g.-mol. H_2O_2/min.)	10^5 × Rate, observed (g.-mol. H_2O_2/min.)
Fig. 1, 5·5 c.c. H_2SO_4 after 10 min. reaction	7·5	1·72	8·95	9·7	8·2
Fig. 5, 10·0 c.c. H_2O_2 after 13 min. reaction	6·52	1·56	10·10	8·6	6·2
Fig. 3, 4·0 c.c. $NaNO_2$ after 9·5 min. reaction	4·7	1·56	4·55	2·8	2·5
Fig. 5, 5·0 c.c. H_2O_2 after 15 min. reaction	4·6	1·56	4·71	2·8	3·2

The reaction mixture and bromide ion.

The mixture liberates bromine from hydrobromic acid, the amount rising with an increase in the ratio $HNO_2 : H_2O_2$, up to a maximum, and thereafter falling, because bromine reacts with nitrite, finally to zero. In investigating the stoicheiometry in the presence of hydrobromic acid, several factors have to be taken into account. First, since the reaction between sodium nitrite and hydrogen peroxide in an appreciable acidity is extremely fast, the bromide must be present initially. Secondly, since bromine is liberated from hydrobromic acid by hydrogen peroxide of even moderate strength its concentration must be kept low. Thirdly, since bromine is reduced fairly rapidly by nitrous acid, the nitrite must be added dropwise to acidified hydrogen peroxide–bromide to ensure that the major part of it reacts with the peroxide. Reproducible determinations of bromine could not be made with the "Spekker" photo-absorptiometer owing to the photochemical reaction between bromine and hydrogen peroxide, but concordance resulted from extraction of the bromine with carbon tetrachloride and titration of its equivalent iodine with thiosulphate. Actually, solutions containing 5 c.c. of hydrogen peroxide of known strength, 5 c.c. of 4N-sulphuric acid, and 5 c.c. of 10% potassium bromide solution in 25 c.c. of water were severally treated dropwise with 1, 2, 3, etc., c.c. portions of the sodium nitrite, and the bromine, extracted with 25 c.c. of carbon tetrachloride, was determined. The residual hydrogen peroxide was also determined. The results, Table 5, indicate that the ratios $H_2O_2 : NaNO_2$ in columns 2, 3, and 4 vary with experimentation and always decrease as the nitrite increases.

Table 5, section *A*, shows that the bromine content continues to increase with nitrite addition so long as any peroxide remains. Thereafter, nitrite reacts with the bromine. Column 2 gives the g.-mols. of peroxide used (per g.-mol. of nitrite), and column 3 the g.-mols. of peroxide (per g.-mol. of nitrite) equivalent to the bromine. The difference between the total peroxide used and the amount equivalent to the bromine liberated is given in column 4. If we make the probable assumption that this peroxide is used in oxidising the nitrite to nitrate, and, provided that the peroxide is in excess, the ratio peroxide : nitrite approximates to unity in Table 5 section *A*, but is higher in sections *B* and *C*, suggesting some evolution of oxygen with higher concentrations of peroxide.

TABLE 5.

Column headings : 1, $NaNO_2$ added (c.c.).
2, G.-mols. of H_2O_2 per g.-mol. of $NaNO_2$.
3, Br liberated, calc. as g.-mols. of H_2O_2 per g.-mol. of $NaNO_2$.
4, G.-mols. of H_2O_2 reacting with 1 g.-mol. of $NaNO_2$ (col. 2 — col. 3).

(1)	(2)	(3)	(4)	(1)	(2)	(3)	(4)
	Section A.				*Section* B.		
1·0	2·85	1·83	1·02	1·0	3·27	1·90	1·37
2·0	2·48	1·52	0·96	2·0	2·89	1·78	1·11
3·0	2·48	1·53	0·95	3·0	2·69	1·55	1·14
3·3	2·43	1·43	1·00	4·0	2·61	1·54	1·07
3·6	2·23	1·26	0·97				
4·0	2·01	1·10	0·91		*Section* C.		
5·0	1·61	0·73	0·88	5·0	3·25	1·72	1·53
6·0	1·34	0·40	0·94	10·0	2·95	1·64	1·31
				20·0	2·43	1·21	1·22

In section *A*, 1% $NaNO_2$ solution, 0·472N-H_2O_2; CCl_4 added after the reaction was completed. In section *B*, 1% $NaNO_2$ solution, 0·87N-H_2O_2; CCl_4 present throughout. In section *C*, as in *B* except that 0·1% $NaNO_2$ solution was used.

The formation of pernitrous acid in the reactions of hydrogen peroxide with nitrous acid, nitrogen dioxide, and nitric oxide.

Some observations have been made on the transient yellow coloration in acid solution noted by Trifonow. First, it was found that when dilute peroxide is added to nitrite there is little or no evolution of oxygen; but when the order of addition is reversed oxygen is liberated, the amount increasing with the concentration of the hydrogen peroxide. Secondly, we observed the transient yellow colour by a flow method: hydrogen peroxide–sodium nitrite, flowing through a long glass tube, met at a side arm dilute hydrochloric acid which caused a yellow band to appear in the main stream and extend from just beyond the confluence to a point about 10 cm. further along the tube; the extension varied with the rate of flow. Estimated from the flow rate and the extension of the colour, the life of the pernitrous acid from the mixture used was between 2 and 3 seconds. The yellow liquid, when run into excess of sodium hydroxide, gave a bright yellow colour, stable for many hours. Just beyond the yellow band a vigorous evolution of oxygen took place, but the colourless liquid gave no colour whatsoever when made alkaline. For more detailed examination, the reactants were run down an open " Perspex " trough, instead of a glass tube, so that reagents could be added at any point. Thus it was shown that much bromine was liberated from potassium bromide introduced at any point within the yellow band. When added just beyond the yellow band, however, only a trace of bromine was set free. Hence the oxidation of the bromide ion is probably exclusively due to the pernitrous acid, and not to products resulting from its decomposition.

As might be expected, solutions of the fairly stable, yellow sodium pernitrite result from the rapid addition of acidified peroxide to alkalified nitrite, or when either nitric oxide or nitrogen dioxide is passed into alkaline hydrogen peroxide. The formation of pernitrous acid when nitric oxide reacts with hydrogen peroxide appears not to have been observed before, although it is well known that nitric oxide is oxidised, eventually, to nitric acid, by this treatment. Passing nitric oxide, free from nitrogen dioxide, into alkaline hydrogen peroxide in complete absence of oxygen, gave a yellow colour. The concentration of both sodium hydroxide and hydrogen peroxide was kept low to avoid liberation of oxygen.

We also showed that pernitrous acid is formed, even in acid solution, by bubbling nitric oxide through an acidified solution of hydrogen peroxide and potassium bromide. Much bromine was liberated, which is characteristic of pernitrous acid, whereas no bromine appeared in the absence of hydrogen peroxide and only a trace in the absence of nitric oxide.

Free radicals in reactions involving pernitrous acid.

Reaction between Hydrogen Peroxide and Sodium Nitrite.—The characteristics of the reaction, particularly in the presence of bromide ion, and the evolution of oxygen with certain concentrations of peroxide suggested the possible formation of free radicals. We have demonstrated their occurrence by observing the polymerisation of unstabilised methyl acrylate (Fryling, U.S.P. 2 378 694, states that " peroxynitric acid " initiates the co-polymerisation of diene hydrocarbons and methylene cyanides; this is of interest, but, from the description, his material did not contain pernitrous acid). To a mixture of 10 c.c. of 2% hydrogen peroxide, 1 c.c. of 4N-hydrochloric acid, and 3 c.c. of saturated aqueous methyl acrylate solution in 40 c.c. of water, mechanically stirred and deaërated with a stream of nitrogen, was added drop by drop 5% sodium nitrite solution, also deaërated. The solution became opalescent almost immediately. Polymerisation also occurred with 2 c.c. instead of 3 c.c. of the monomer, but not when the amount of added monomer was reduced to 1 c.c. The associating effect, although evident, was less when the peroxide was added dropwise to acidified nitrite and methyl acrylate. Thus a mixture of 10 c.c. of 5% sodium nitrite solution, 1 c.c. of 4N-hydrochloric acid, and 3 c.c. of saturated aqueous methyl acrylate solution in 40 c.c. of water, stirred and deaërated with nitrogen gave no visible polymerisation when treated, dropwise, with 10 c.c. of 2% deaërated hydrogen peroxide. Nevertheless, with 5 c.c. of monomer present, opalescence appeared towards the end of the addition of the peroxide. But with excess of nitrous acid there was no polymerisation; a deaërated mixture of 10 c.c. of 2% hydrogen peroxide, 10 c.c. of 5% sodium nitrite solution, and 5 c.c. of saturated aqueous monomer solution in 40 c.c. of water was acidified by the rapid addition of dilute hydrochloric acid without evincing evidence of any polymerisation, only the transient yellow colour of the pernitrous acid being observed. Nor did polymerisation take place when very dilute acid was added dropwise to this mixture. Blank experiments omitting each of the three reagents in turn gave no polymerisation.

Reaction between Hydrogen Peroxide and Nitric Oxide or Nitrogen Dioxide.—No polymerisation was met when either nitric oxide or nitrogen dioxide was passed into the acidified monomer solution, but, in the presence of hydrogen peroxide, rapid polymerisation occurred with either oxide of nitrogen, caused, presumably, by pernitrous acid. Polymerisation did not occur when nitric oxide was passed into monomer in alkaline hydrogen peroxide, only the yellow colour of sodium pernitrite being observed.

Acidification of Sodium Pernitrite Solutions.—Various evidence points to the decomposition of pernitrous acid as the source of the free radicals. We have demonstrated their formation by this means by preparing aqueous sodium pernitrite, in the complete absence of hydrogen peroxide, and liberating therefrom pernitrous acid in the presence of methyl acrylate. For this purpose, aqueous sodium azide was ozonised to give sodium pernitrite (method of Gleu and Roell, *loc. cit.*). M-Sodium azide solution was ozonised until azide could no longer be detected with silver nitrate, at which stage, according to Gleu, only sodium pernitrite, nitrite, and nitrate are present. The solution, when deaërated and acidified under air-free conditions, caused the polymerisation of methyl acrylate.

Reaction of the free radicals with benzene.

By using Pernitrous Acid from Hydrogen Peroxide and Nitrous Acid.—The experiments with methyl acrylate showed that excess of nitrous acid must be avoided since it appears to react with either the pernitrous acid or the products of its decomposition. The concentration of hydrogen peroxide must also be kept low as it competes for reaction with the radicals. (N.B. Neither nitrous acid alone nor hydrogen peroxide and unacidified nitrite in the concentrations used affect benzene.) Hence for interaction with benzene a mixture of hydrocarbon (100 c.c.), 5% hydrogen peroxide solution (100 c.c.), 3N-hydrochloric acid (5 c.c.), and water (250 c.c.) was emulsified in a 750-c.c. round-bottomed flask, and 5% sodium nitrite solution (150 c.c.) was added dropwise. All the materials were at room temperature and stirring was continued throughout the addition (about 30 minutes). The molecular ratio hydrogen peroxide : nitrous acid was about 1·5 : 1, thus maintaining the former always in excess. At the end of the run the emulsion was allowed to separate into an aqueous and a benzene layer; both were deep yellowish-brown. Material from twenty such runs on redistilled thiophen-free benzene having been collected, the organic layer was extracted with dilute sodium hydroxide solution until the extract was colourless, washed with water, dried (Na_2SO_4), and distilled under reduced pressure to remove unchanged benzene. The dark brown liquid left (10·5 g.), on fractional distillation, yielded nitrobenzene (10 g.), b. p. 209°, and a small tarry residue.

The residue was sublimed in a vacuum, and the sublimate was separated into two fractions by controlled resublimation. The first fraction, recrystallised from aqueous alcohol, consisted of pure white crystals of diphenyl, m. p. 69°. The mixed m. p. with authentic diphenyl was 69·5°. The second fraction of the sublimate remained yellow when recrystallised from absolute alcohol, had m. p. 172—173°, and proved to be *p*-dinitrobenzene (mixed m. p. 173°).

The alkaline extract of the benzene layer was acidified with concentrated hydrochloric acid and extracted with ether. After drying of the extract and removal of the ether, a dark tarry residue (5·0 g.) remained. Steam-distillation gave crude *o*-nitrophenol (3·25 g.) which, when purified by vacuum-distillation and recrystallisation from aqueous alcohol, had m. p. 45°, not depressed by the authentic compound. The crude *o*-nitrophenol appeared to contain a trace of 2 : 4-dinitrophenol. The tarry residue from the steam-distillation did not sublime in a vacuum but dissolved in hot 6N-sodium hydroxide, from which, on cooling, a small amount of a deep red sodium salt crystallised. Further evaporation and cooling yielded a small amount of a yellow sodium salt. On acidification and extraction with ether the red salt gave a deep yellow phenol, m. p. 68—69°. Reduction with tin and hydrochloric acid produced a very small amount of a light brown, solid amine which became almost white after recrystallisation from chloroform. Its m. p., 200—206°, indicates that it is 3-amino-4-hydroxydiphenyl (m. p. 208°); the nitro-compound was thus 3-nitro-4-hydroxydiphenyl (m. p. 67—68°). The yellow sodium salt on acidification and extraction with ether yielded a very small amount of *p*-nitrophenol which, recrystallised from light petroleum, had m. p. 110—114° slightly raised by admixture with the authentic compound (m. p. 114°).

The original aqueous layer from the reaction was extracted with ethyl acetate. The extract, dried and distilled to remove ethyl acetate, left a tarry residue. Its distillation in a vacuum yielded a small amount of yellow oil, proved qualitatively to be a mixture of *o*-nitrophenol and phenol. Though not readily separated the presence of phenol was demonstrated both by the formation of phenolphthalein with phthalic anhydride, and by the positive reaction to Liebermann's test for phenol.

To sum up, the products were nitrobenzene (10 g.), *o*-nitrophenol (3·25 g.), and, in much smaller quantity, diphenyl, *p*-dinitrobenzene, *p*-nitrophenol, and 3-nitro-4-hydroxydiphenyl. Some evidence has also been obtained for the presence of phenol and 2 : 4-dinitrophenol.

By using Pernitrous Acid from Sodium Azide.—Sodium pernitrite was prepared by ozonising M-sodium azide (200 c.c.), and the orange alkaline solution was emulsified with benzene (100 c.c.) and acidified by adding 3N-hydrochloric acid drop by drop. The benzene and the aqueous layer, both light yellow, were worked up and the former yielded indubitable evidence of nitrobenzene and *o*-nitrophenol. The small yield obtained is believed to be due to the unavoidable presence of so much sodium nitrite which, by producing nitrous acid, tends to destroy much of the pernitrous acid. However, as Gleu and Roell (*loc. cit.*) have shown that a completely ozonised M-azide solution is approximately 0·3N in respect to active oxygen and 0·15M in respect to nitrite, we were able to compare these yields with those derived from peroxide-produced pernitrous acid, in the presence of a similar relative concentration of nitrite. For this purpose, benzene (100 c.c.), hydrogen peroxide (3·4 g.), and sodium nitrite (13·8 g.) in water (200 c.c.) were emulsified. The aqueous portion was thus N with respect to active oxygen and M with respect to nitrite; and, since 1 g.-mol. of hydrogen peroxide reacts with 1 g.-mol. of nitrous acid to form pernitrous acid, these conditions provide the same ratio of pernitrous acid to nitrite as was in the ozonised azide solution, but at concentrations about three times greater. Acidification of the emulsion with 3N-hydrochloric acid produced a yellow colour in both the benzene and the aqueous layer, the colour being only slightly deeper than observed with the ozonised azide. The products of the reaction were isolated and the yields of both nitrobenzene and *o*-nitrophenol proved to be of the same order as those from the ozonised azide.

By using Pernitrous Acid from Nitric Oxide.—A qualitative examination of the materials produced when pure nitric oxide is passed into an emulsion of 5% hydrogen peroxide solution (30 c.c.), water (55 c.c.), 6N-hydrochloric acid (1 c.c.), and benzene (20 c.c.), under air-free conditions, showed the usual products, but, in addition, nitrosophenols were also present.

DISCUSSION

We have shown that the reaction between hydrogen peroxide and nitrous acid is independent of nitrite and directly proportional to nitrous acid and to hydrogen peroxide concentrations. The reaction is markedly acid-catalysed. With pernitrous acid as an intermediate the overall reaction has been shown to be

$$HNO_2 + H_2O_2 \longrightarrow HNO_3 + H_2O$$

Evidently from the polymerisation experiments and the array of organic reactions recorded in the following paper free radicals are produced at some stage. We have been at some pains to define as closely as possible where, when, and how these arise. Early suspicions that the free radicals originated in the hydrogen peroxide seemed to be excluded by the fact that the phenomena observed are associated in time and place with the transient brownish-yellow pernitrous acid and are completely ruled out by the fact that they are formed in the absence of hydrogen peroxide. Especially we regard as significant that acidified sodium pernitrite (from azide) produces from benzene an amount of *o*-nitrophenol similar to that produced by an equivalent mixture of nitrite and peroxide. These considerations lead us to favour a scheme in which radicals appear, not in the formation of the pernitrous acid, but in its decomposition :

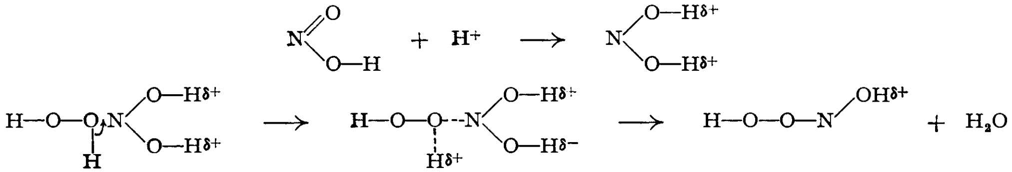
$$NO_2^- + H^+ \longrightarrow HNO_2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

$$HNO_2 + H_2O_2 \longrightarrow HO_2NO + H_2O \quad . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

$$HO_2NO \longrightarrow HO + NO_2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

$$HO + NO_2 \longrightarrow HNO_3 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

At low acidities (3) is the rate-determining stage and might be regarded from an esterification angle :



$$HO_2NOH^{\delta+} \longrightarrow HO_2NO + H^+$$

At higher acidities (0·1—0·2N), the rate of formation of pernitrous acid is so fast as to colour the solution and if then the ion NO$^+$ should appear (which we think extremely unlikely), an alternative mechanism not excluded is :

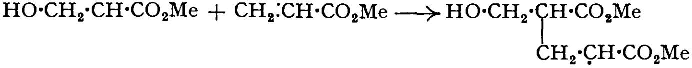
$$HNO_2 + H^+ \rightleftharpoons H_2O + NO^+$$
$$NO^+ + H_2O_2 \longrightarrow HO_2NO + H^+$$

When hydrogen peroxide is abundant the hydroxyl radicals provide a means of oxygen liberation by such a chain as

$$HO + H_2O_2 \longrightarrow H_2O + HO_2$$
$$H_2O_2 + HO_2 \longrightarrow HO + H_2O + O_2$$

The polymerisation of methyl acrylate may be presumed to follow from the normal functioning of hydroxyl radicals :

$$CH_2{:}CH{\cdot}CO_2Me + {\cdot}OH \longrightarrow HO{\cdot}CH_2{\cdot}\dot{C}H{\cdot}CO_2Me$$



$$HO{\cdot}CH_2{\cdot}\dot{C}H{\cdot}CO_2Me + CH_2{:}CH{\cdot}CO_2Me \longrightarrow HO{\cdot}CH_2{\cdot}\underset{CH_2{\cdot}\underset{\cdot}{C}H{\cdot}CO_2Me}{\underset{|}{C}H}{\cdot}CO_2Me$$

and the fact that a certain minimum concentration of monomer is necessary finds ready explanation when the chain-breaking properties of the second free radical NO$_2$ are recalled :

$$HO{\cdot}CH_2{\cdot}\dot{C}H{\cdot}CO_2Me + NO_2 \longrightarrow HO{\cdot}CH_2{\cdot}CH(NO_2){\cdot}CO_2Me$$

We believe the reduction in polymerisation and hydroxylation, found when high concentrations of nitrous acid are present, to be due to the destruction of the per-acid by reduction as it is formed.

When bromide ion is present it is oxidised by the per-acid to bromine. In our view the results in Table 5 confirm the following reaction stages which, while not identical with, are related to a scheme suggested by Gleu to explain the presence of free bromine in the solution at the end of the reaction :

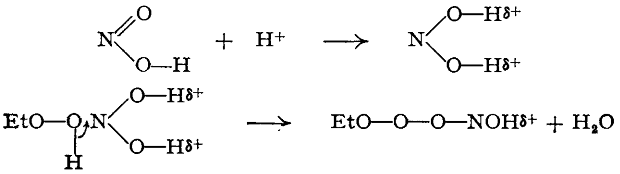
$$H_2O_2 + HNO_2 \longrightarrow HO_2NO + H_2O \quad . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$
$$HO_2NO + 2HBr \longrightarrow Br_2 + H_2O + HNO_2 \quad . \; . \; . \; . \; . \; . \; . \quad (7)$$
$$HO_2NO \longrightarrow HNO_3 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (8)$$
$$HNO_2 + Br_2 + H_2O \longrightarrow HNO_3 + 2HBr \quad . \; . \; . \; . \; . \; . \; . \; . \quad (9)$$

The figures in columns 3 and 4 of Table 5 are then a measure of stages (7) and (8) respectively; their ratio gives a rough idea of the relative rate of these two reactions at the concentrations used. The decrease in peroxide reacting and in bromine liberated (per g.-mol. of nitrite) observed as the amount of nitrite is increased is evidently caused by the prominence of process (9) at higher concentrations of free bromine. Some bromine may arise by the intervention of the hydroxyl radical (that the electron transfer $OH + Br^- \longrightarrow Br + OH^-$ is possible was demonstrated by the strong discharge of bromide ion which took place when we added dilute ferrous sulphate to an acidified peroxide–bromide mixture), but tests made during the flow experiment led us to believe that most of the oxidation should be ascribed to the per-acid itself. The maximum liberation of bromine occurs just at the point where all the hydrogen peroxide has been used up. The actual ratio of hydrogen peroxide to nitrous acid used at this point depends on the relation of the several competing reactions and is not, as Trifonow (*loc. cit.*) assumed, the stoicheiometric one for the formation of pernitrous acid.

The formation of alkyl nitrates by the reaction between ethyl hydroperoxide and alkyl nitrites has been explained by Baeyer and Villiger (*loc. cit.*) as due to the formation of an intermediate addition compound. The postulated mechanism for the reaction between hydrogen peroxide and nitrous acid appears to indicate, however, that the main processes occurring in Baeyer's reaction may be :

$$EtO{\cdot}NO + H_2O \longrightarrow EtOH + HNO_2$$

followed by



$$EtO—\overset{\curvearrowright}{O}—N—OH^{\delta+} \longrightarrow EtO\cdot + NO_2 + H^+$$
$$EtO\cdot + NO_2 \longrightarrow EtO{\cdot}NO_2$$

These stages are not incompatible with the products isolated by Baeyer and Villiger and it is notable that when these workers substituted hydrogen peroxide for the ethyl hydroperoxide the products contained no alkyl nitrate but some aldehyde. In this case we should expect pernitrous acid which would be capable of oxidising the alcohol to aldehyde.

Not much may be usefully said of the recent paper by Abel (*loc. cit.*) since it is based on the assumption that the yellow compound herein described is a solution of nitrogen dioxide in water. Actually nitrogen dioxide dissolves in water to give a colourless solution and, indeed, only shows its colour when in the form of gas either in the bubbles within the saturated aqueous solution or above it. Of the difference between an aqueous solution of nitrogen dioxide and pernitrous acid the present writers have no doubt.

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