Evidence of a Branched Chain Reaction in the Oscillating Reaction of Hydrogen Peroxide, Iodine and Iodate

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The oscillating chemical reaction in a solution of KIO_3, H_2O_2, and H_2SO_4 was studied by recording the light absorption due to dissolved iodine. The measurements were reproducible and the reaction was not influenced by stirring. At high H_2O_2 concentrations the reaction proceeds without oscillation. The oxidation of I_2 by H_2O_2 is strongly influenced by halogenides and unsaturated organic compounds. The reduction of HIO_3 by H_2O_2 is not influenced by these substances. H_2O_2 is an inhibitor in the oxidation of iodine by H_2O_2. This oxidation is assumed to take place by a free radical chain reaction. The oscillation is a result of quadratic branching in the chain reaction.

The possibility of an oscillatory behaviour of a chemical reaction has been a matter of controversy. Some experimental evidence, namely the reaction of hydrogen peroxide and potassium iodate in dilute sulfuric acid, as described by Bray [1] many years ago, suggests that oscillating reactions exist in the homogeneous phase. More recently, Belousov [2] has found a sustained oscillation in a solution of malonic acid, ceric sulfate, and potassium bromate in dilute sulphuric acid. This reaction has been studied further by Zhabotinskij [3] and Degn.[4] There seems to be no reason to doubt its homogeneity. In addition to the two reactions mentioned above an oscillating enzymic reaction has also been reported. Chance et al.[5] found oscillations of the NADH concentration in a cell free extract of yeast.

After Bray's original work the hydrogen peroxide-iodate reaction has been reinvestigated twice. In both cases it was concluded that the reaction is not homogeneous.

Rice and Reiff [6] found that the periodicity disappeared when the hydrogen peroxide was distilled. They ascribed the periodicity to the presence of dust particles. Peard and Cullis [7] suggested that the oscillation was due to physical removal of iodine by the evolving oxygen. The experiments to be described in

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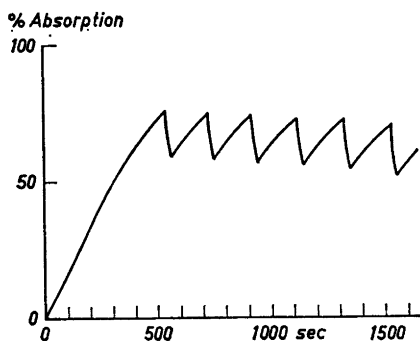
Fig. 1. Light absorption as a function of time in 10 ml of the standard solution + 200 μl of 30 % H_2O_2 at wavelength 460 mμ.

the present paper indicate that neither of the explanations assuming inhomogeneity in the hydrogen peroxide-iodate reaction is correct. It is concluded from the experiments that the oscillation is caused by a free radical branched chain reaction which starts and stops abruptly when critical concentration boundaries are reached.

Experiment I. Verification of the oscillation. This experiment was, as all the following ones, performed in an 11 ml cuvette of a Zeiss spectrophotometer. The temperature was 65°C, and the light absorption was measured at 460 mμ where the light absorption of iodine has a maximum. There was vigorous mechanical stirring. A solution which was 0.15 N with respect to H_2SO_4 and 0.046 M with respect to KIO_3 was used. This solution will be referred to as the standard solution. To 10 ml of the standard solution was added 200 μl of 30 % (9.8 M) hydrogen peroxide (Perhydrol, Merck), and the light absorption was recorded as a function of time. The resulting curve is shown in Fig. 1. During the experiment an evolution of oxygen was seen. This became very vigorous after each of the rapid falls in the iodine concentration. About 60 periods were observed before the reaction came to an end. The duration of the period increased with time, and the maximum iodine concentration in the period decreased with time. At the end there was practically no iodine left in the solution. The experiment was repeated with distilled hydrogen peroxide and with sodium peroxide as a substitute for hydrogen peroxide. In both cases the reaction oscillated. When sulfuric acid was substituted by phosphoric or perchloric acid, adjusting to the same pH as in the standard solution, the reaction was still oscillating. This was not the case when nitric or hydrochloric acid was used. Stirring was found to have no influence on the oscillating reaction. The role of stirring in the experiments was to prevent oxygen bubbles, interfering with the measurements, from sticking to the glass walls.

An inspection of the curve in Fig. 1 reveals that the oscillation is not of a sinusoidal nature. It appears to be a relaxation oscillation. An oscillation of this type may occur when two processes are connected in such a way that a quantity A, produced by process (I), is consumed partially or fully by process (II) when A exceeds a critical value. Physical examples of relaxation oscillators which operate according to this principle are the glow discharge lamp oscillator and the dripping water tap. In the former example process (I) is the accumulation of charge on a condenser and process (II) is the discharge of the condenser through a glow discharge lamp, occurring when a critical potential has been reached. The potential-time curve of this oscillator is virtually identical with the curve in Fig. 1.[8] In the latter example process (I) is the

accumulation of water in the hanging drop and process (II) is the release of the drop, occurring when a critical weight has been reached.

If the present chemical reaction conforms with the above general scheme of relaxation oscillations the sections of the curve which have a positive slope must represent the production phases (I), and the sections which have negative slopes must represent the consumption phases (II).

Iodine is produced by the reduction of iodate by hydrogen peroxide

$$2HIO_3 + 5H_2O_2 = I_2 + 5O_2 + 6H_2O \tag{I}$$
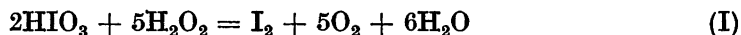
and is consumed by the oxidation of iodine by hydrogen peroxide

$$I_2 + 5H_2O_2 = 2HIO_3 + 4H_2O \tag{IIa}$$

However, this reaction scheme does not explain that most of the oxygen is evolved in connection with the consumption reaction (II). To explain this fact it is necessary to assume that reaction (IIa) is accompanied by a dismutation of hydrogen peroxide

$$2H_2O_2 = 2H_2O + O_2 \tag{IIb}$$

In the present experiments only reaction (IIa) was followed since the iodine absorption and not the oxygen evolution was measured.

Reaction (IIa + b) has the notable property that it can be at rest when the reactants are present in substantial concentrations and only initiate when a critical concentration of a reactant is reached. Branched chain reactions are known to have this property. It is, therefore, suggested that reaction (IIa + b) is a branched chain reaction. An interplay of a reaction continuously producing iodine and a branched chain reaction consuming iodine when a critical concentration of this substance is reached does not necessarily lead to a sustained oscillation. According to Lotka's theoretical treatment of a reaction scheme of this type only a damped oscillation may occur. This subject is treated in the discussion. At present we shall seek evidence for the assumption that reaction (IIa + b) is at rest during the phase ascribed to reaction (I).
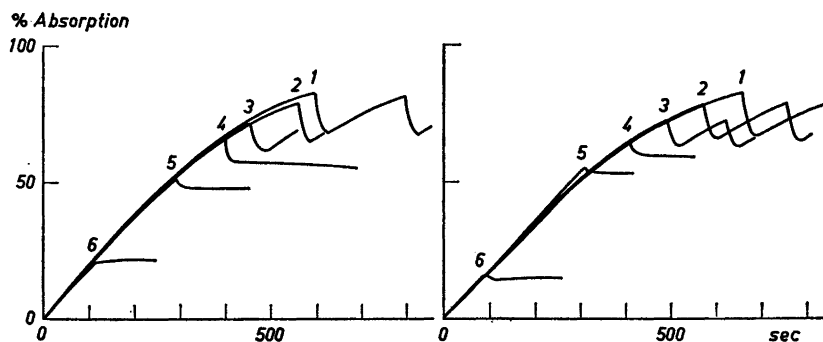

Fig. 2. Effect of chloride and bromide on the oscillating reaction. Besides standard concentrations of KIO_3 and H_2SO_4 the solutions are: (1) 0, (2) 6, (3) 15, (4) 30, (5) 60, and (6) 300 μM with respect to KCl (left curve) and KBr (right curve). 250 μl or 30 % H_2O_2 was added to 10 ml of solution.
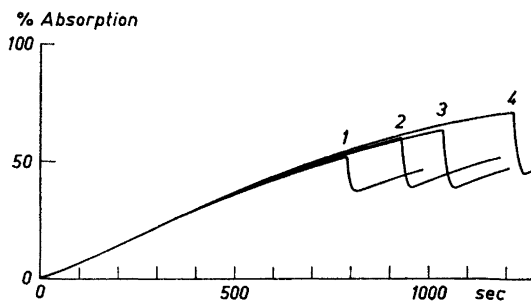
Fig. 3. Effect of fluoride on the oscillating reaction. Besides standard concentrations of KIO$_3$ and H$_2$SO$_4$ the solutions are: (1) 0, (2) 150, (3) 300, and (4) 600 μM with respect to NaF. 100 μl of 30 % H$_2$O$_2$ was added to 10 ml of solution.

Experiment II. Influence of halogenides. To 10 ml of the standard solution was added a small amount of KCl or KBr and 200 μl of 30 % hydrogen peroxide. The light absorption of iodine was recorded as a function of time. The experiment was also performed with NaF and 100 μl of 30 % hydrogen peroxide. The resulting curves are shown in Figs. 2 and 3. It is seen that the addition of increasing amounts of chloride or bromide resulted in decreasing maximum values of the iodine concentration. When NaF was used the maximum iodine concentration increased with the fluoride concentration. In all cases, when halogenides were added, the curves before the first maximum were identical within the experimental error.

It is concluded from these experiments that reaction (II), the oxidation of iodine, does not proceed at all time, since if this occurred, its sensitivity to halogenides would be reflected in the whole curve. It was noticed by Bray[1] that chloride had a strong influence on the overall reaction. It appears that this influence is restricted to the oxidation of iodine. The reduction of iodate is not affected. Chloride and bromide catalyse reaction (II), whereas fluoride is an inhibitor of this reaction.

If the chain reaction hypothesis is adopted the inflection point must indicate the critical concentration of iodine where the branching factor passes from negative to positive (see discussion). In other words, the branching factor depends on the fluoride, chloride, and bromide as well as the iodine concentration. It is noted from Fig. 1 that the critical iodine concentration decreases with time. This means that the branching factor depends on a concentration which is monotonically changing with time. Probably this is the hydrogen peroxide concentration.

Experiment III. Influence of the hydrogen peroxide concentration. Expt. I was repeated with varying amounts of hydrogen peroxide. The resulting curves are shown in Fig. 4. It is seen that the rate of formation of iodine was increased and the maximum appeared at higher iodine concentrations when the hydrogen peroxide concentration was increased. At high concentrations of hydrogen peroxide there was no oscillation, but the maximum was followed by a rather stationary phase with a slowly decreasing iodine concentration. After a while the oscillation started. When the reaction was in the non-periodic phase the addition of a minute amount of hydrogen peroxide caused an immediate upward inflection of the curve and one period of oscillation was produced (Fig. 7). Thereafter the non-periodic phase went on.
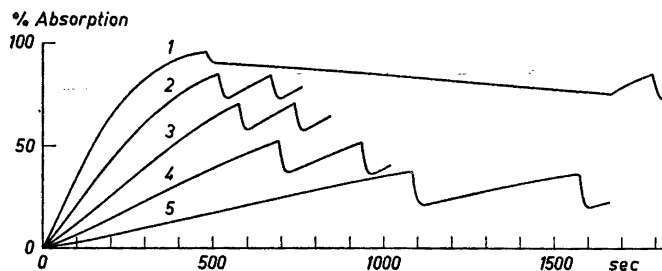
Fig. 4. Effect of hydrogen peroxide concentration on the oscillating reaction. (1) 500, (2) 300, (3) 200, (4) 100, and (5) 50 μl of 30 % H_2O_2 was added to 10 ml of the standard solution. In the cases 2—5 the volume was made up to 10.5 ml with water.

When the critical iodine concentrations determined in expt. III are plotted against the initial hydrogen peroxide concentrations the curve shown in Fig. 5 is produced. Assuming that the hydrogen peroxide concentration did not decrease significantly from the beginning of the experiment to the first maximum, this curve pictures all the pairs of I_2 and H_2O_2 concentrations for which the branching factor is zero. The curve is nearly a straight line through (0,0). It follows from this experiment that the critical concentration of iodine is related to the hydrogen peroxide concentration by the linear equation $[I_2] = 1.8 \times 10^{-3} [H_2O_2]$. Hydrogen peroxide is an inhibitor of the branched chain reaction although it is a reactant in this reaction.

The non-periodic phase at high hydrogen peroxide concentrations is supposed to exist because reaction (II) is repressed but not totally interrupted. There is a steady state where iodine production by reaction (I) is balanced by iodine consumption by reaction (II). If this is correct the non-periodic phase gives a good opportunity to study the properties of reaction (II). Under the normal oscillation this reaction is only in function for a few seconds at a
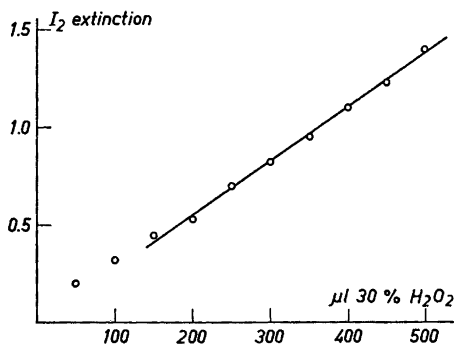

Fig. 5. Iodine extinction at first inflection (expt. III, Fig. 4) plotted against initial amount of H_2O_2.
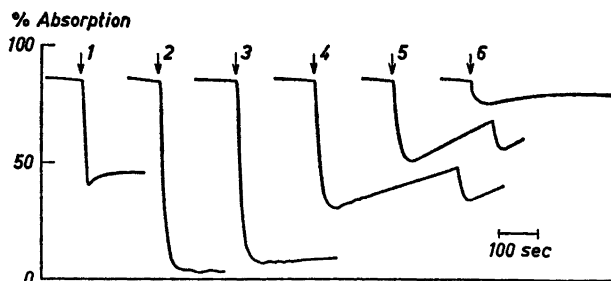
Fig. 6. Reaction between hydrogen peroxide and preformed iodine. Iodine was evolved in 10 ml of standard solution by adding 25 μl of 0.4 M KI. In cases 1—4 100 μl of 0.6, 3, 15, and 30 % H_2O_2 was added. In the cases 5 and 6, 200 and 400 μl of 30 % H_2O_2 were added, respectively.

time. The interruption of the non-periodic phase by addition of hydrogen peroxide demonstrates the inhibitory effect of hydrogen peroxide on reaction (II).

It was also desirable to study the reaction between iodine and hydrogen peroxide at low concentrations of the latter substance. This was done by adding hydrogen peroxide to solutions where iodine had been evolved beforehand by the reaction between iodide and iodate.

Experiment IV. Reaction between preformed iodine and added H_2O_2. 25 μl of 0.4 M KI were added to 10 ml of the standard solution. Following this a small amount of hydrogen peroxide was added, and the light absorption of iodine was recorded as a function of time. The experiment was repeated with varying amounts of H_2O_2. The resulting curves are shown in Fig. 6. After the addition of hydrogen peroxide there was a short induction period followed by a rapid fall of the iodine concentration. When very small amounts of hydrogen peroxide were used the iodine concentration fell down to a minimum after which it was partially restored. When a somewhat higher H_2O_2 concentration was used the iodine disappeared almost completely and did not show up again. At high concentrations of hydrogen peroxide the depth of the minimum decreased with increasing H_2O_2 concentrations. When the order of addition of KI and H_2O_2 was reversed the rapid formation of iodine by oxidation of I^- was followed by a short induction period and the curve developed exactly as before.

The inhibiting effect of hydrogen peroxide on reaction (II) is clearly seen from the experiment. The induction period of the reaction is well known.[9] One unexpected finding is the minimum of the curve when very small amounts of hydrogen peroxide are used. This may be interpreted as follows. When the amount of hydrogen peroxide is very small this substance will be consumed completely by the chain reaction because there is no inhibition from H_2O_2. When the chain reaction proceeds there is a high concentration of chain centre, and this concentration is still considerable when all the hydrogen peroxide has been consumed and the chain reaction therefore has stopped. The regeneration of iodine is a result of recombination or dismutation of chain centre after the cessation of the chain reaction. The unknown species which regenerates iodine must be present in a concentration of at least 50 μmolar as calculated
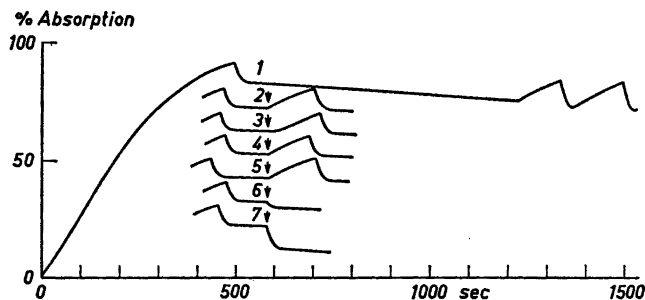
Fig. 7. Influence of unsaturated organic compounds and other substances on the non-periodic phase. Case 1 is the normal curve. In the other cases the following substances were added: (2) 5 μl of 1 % acrylamide, (3) 5 μl of 2 % acrylonitrile, (4) 5 μl 30 % H_2O_2, (5) 10 μl 2 % NaF, (6) 5 μl 0.1 % KCl, and (7) 25 μl 0.1 % KCl.

from the minimum and final iodine extinctions. If it is a free radical it may therefore be possible to detect it by means of ESR-spectroscopy. However, different attempts to do so were unsuccessful. The classical way of detecting free radical intermediates in chain reactions is based on the pronounced tendency of free radicals to react with unsaturated organic compounds. Such substances are powerful inhibitors of free radical chain reactions, whereas they do not markedly affect reactions with nonradical intermediates.

Experiment V. Influence of unsaturated organic compounds. 400 μl of 30 % hydrogen peroxide was added to 10 ml of the standard solution. When the non-periodic stationary phase found in expt. III was reached 5 μl of 1 % acrylamide was added. There was seen an immediate upward inflection of the iodine absorption curve and one period of oscillation was produced. The addition of acrylonitrile had the same effect. The effect of adding small amounts of various substances including hydrogen peroxide and halogenides, when the reaction is in the non-periodic phase is illustrated in Fig. 7.

The influence of acrylamide on the reaction between iodine and small amounts of hydrogen peroxide was also tested. The procedure was as described in expt. IV. When a minute amount of acrylamide was added just before the minimum of the curve would normally be reached there was no regeneration of iodine (Fig. 8). When acrylamide
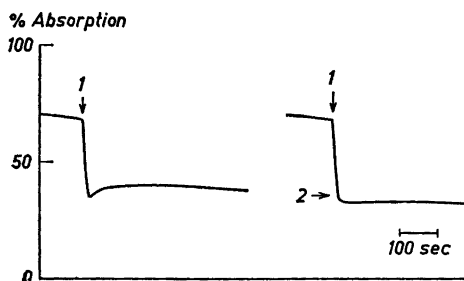

Fig. 8. Effect of acrylamide on the reaction between I_2 and H_2O_2. At 1, H_2O_2 was added to the iodine solution. At 2, 5 μl of 1 % acrylamide was added.

was added to the iodine containing solution without hydrogen peroxide the iodine concentration did not decrease significantly.

The effects of unsaturated organic compounds strongly support the hypothesis that reaction (II) is a branched chain reaction with free radical intermediates. The ability of acrylamide to prevent the regeneration of iodine shows that the intermediate species which normally regenerate iodine is as reactive towards acrylamide as a free radical would be.

DISCUSSION

The above experiments indicate that the oscillations of the chemical system under study is caused by the intermittent action of a branched chain reaction involving free radical intermediates. The presence of free radicals was shown by an unspecific method, and the experimental results do not allow an identification of these radicals. There is, therefore, no basis for suggesting a detailed reaction scheme for the branched chain reaction. We can only discuss the reaction mechanism on a very general level.

According to Semjonow [10] the rate of formation of the chain propagating species (the chain centre) in a branched chain reaction can be written

$$\mathrm{d}n/\mathrm{d}t = n_0 + (f-g)n$$

where n_0 is the slow rate of spontaneous chain initiation. The rates of chain branching and chain termination are both assumed to be proportional to the concentrations of chain centre and the proportionality constants are f and g. The factor $f-g$ is called the branching factor. When the branching factor is negative the reaction rate of the chain reaction is practically zero. When the branching factor is positive the reaction proceeds explosively. The proportionality constants f and g may depend on the concentration of one or more of the reactants, and the sign of the branching factor may, therefore, change from negative to positive when a critical concentration of a reactant is passed.

The following formal reaction scheme is an example of a branched chain reaction fitting the assumptions made in the above theory.

$$A + X \xrightarrow{k_1} 2X$$

$$X \xrightarrow{k_2} B$$

$$C \xrightarrow{k_3} X$$
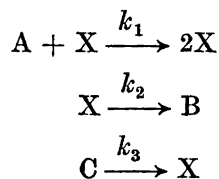
The substance X is the chain centre. The rate of chain centre formation is

$$\mathrm{d}[X]/\mathrm{d}t = k_3[C] + (k_1[A]-k_2)[X]$$

The branching factor is $k_1[A]-k_2$, from which we derive that $[A] = k_2/k_1$ is a critical concentration below which the chain reaction does not proceed. If a zero order reaction supplying A is added to the above scheme we have a reaction scheme which has already been studied by Lotka.[11] He found that [A] would approach the critical value k_2/k_1 through a damped oscillation.

Since the oscillations revealed in the above experiments are undamped, the scheme does not fit the present case.
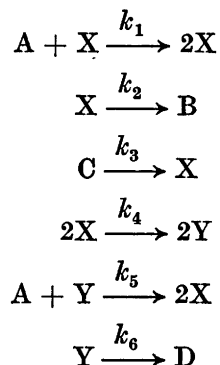
In experiment III it was found that the critical iodine concentration is $[I_2] = 1.8 \times 10^{-3} [H_2O_2]$. An interpretation of this finding would be that the branching factor, in the moment where the chain reaction starts, is governed by the following two reactions

$$I_2 + X \xrightarrow{k_1} 2X$$

$$H_2O_2 + X \xrightarrow{k_2} B$$
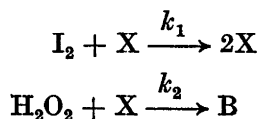
where X symbolizes the chain center which may be more than one species and B is an inert product. The branching factor determined from these reactions is $k_1[I_2] - k_2[H_2O_2]$. Consequently the critical concentration of iodine is $[I_2] = (k_2/k_1)[H_2O_2]$. It is seen that the experimentally determined proportionality constant 1.8×10^{-3} may be interpreted as the proportion of the two rate constants k_2 and k_1.

It may be inferred from the experimental curves that the branched chain reaction which consumes iodine possesses not one but two critical concentrations of iodine, one where the reaction initiates and a lower one where it stops. Such a phenomenon has been observed in connection with a few other branched chain reactions, and according to Semjonow [10] it can be explained by the assumption that the free radicals constituting the chain centre interact to form new radicals which propagate the chain more effectively than the previous ones. Such a mechanism gives rise to a quadratic term in the differential equation describing the rate of chain centre formation. Semjonow named it quadratic branching.

The following formal reaction scheme contains a quadratic branching mechanism in addition to the linearly branched reaction considered above.

$$A + X \xrightarrow{k_1} 2X$$

$$X \xrightarrow{k_2} B$$

$$C \xrightarrow{k_3} X$$

$$2X \xrightarrow{k_4} 2Y$$

$$A + Y \xrightarrow{k_5} 2X$$

$$Y \xrightarrow{k_6} D$$

If the substance A is added continuously the chain reaction will initiate when the critical concentration $[A] = k_2/k_1$ is reached. In the moment where the chain reaction initiates the concentration of X is low, and the reaction $2X \to 2Y$ is, therefore, not significant. However, when the chain reaction has started $[X]$ increases and the reaction $2X \to 2Y$ becomes significant.

At a high concentration of X all newly formed molecules of X will immediately be transformed into Y by this reaction. Under these circumstances the critical concentration of A is k_6/k_5. If $k_2/k_1 > k_6/k_5$ the quadratic branching is positive. The chain reaction will initiate at $[A] = k_2/k_1$ and stop at $[A] = k_6/k_5$. Since A is added continuously its concentration will increase again until $[A] = k_2/k_1$, then the chain reaction will start again etc.

The time evolution of a formal reaction scheme containing a zero order reaction continuously supplying a substance which is consumed by a quadratically branched chain reaction was calculated on a digital computer. The calculation was performed by means of a compiler for chemical kinetics which is described, together with the result of the calculations, in a separate paper.[12] It was found that the reaction scheme produced concentration-time curves which were very similar to the experimental curves from the hydrogen peroxide-iodate system.

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