With the aid of recent data on the mean energy of the peroxide bond \( \text{O} - \text{O} \) \cite{1} it was shown by calculation \cite{2} based on the multiplet theory that hydrogenolysis of peroxy compounds should proceed fairly readily over a nickel catalyst. We will here consider this calculation in greater detail.

The hydrogenolysis of an \( \text{O} - \text{O} \) bond is a thermodynamically possible reaction; its course over nickel can be expressed by a doublet scheme:

\[
\text{H}_2 \quad \text{ Ni} \\
\text{O} - \text{H} - \text{H} (\text{M}) \quad \rightarrow \quad \text{O} - \text{H} \\
\text{O} - \text{H} - \text{H} - \text{O} - \text{H} \\
\text{Ni} \\
\]

If we denote bond energy by \( Q \), then according to the equations of the multiplet theory \cite{3}, the heat of formation of the multiplet complex \( M \) is in the limit given by

\[
E' = -Q_{\text{O-O}} + 2Q_{\text{O-Ni}} - Q_{\text{H-H}} + 2Q_{\text{H-Ni}},
\]

since \( \text{O} - \text{O} \) and \( \text{H} - \text{H} \) bonds are broken and the \( \text{O} \) and \( \text{H} \) atoms are attracted to nickel (see scheme (1)). Similarly, the heat of decomposition of \( M \) is in the limit given by

\[
E'' = 2Q_{\text{O-H}} - 2(Q_{\text{O-Ni}} + Q_{\text{H-Ni}}),
\]

since two \( \text{O} - \text{H} \) bonds are formed in the reaction products and \( \text{O} \) and \( \text{H} \) atoms are torn from the surface.

Substituting in Equations (2) and (3) the values of \( Q \) known from \cite{2} (see Table 1 in [2]), namely \( Q_{\text{O-O}} = 47 \), \( Q_{\text{H-H}} = 104.2 \), \( Q_{\text{O-H}} = 110.6 \), \( Q_{\text{O-Ni}} = 48.5 \), and \( Q_{\text{H-Ni}} = 55 \) kcal, we find that \( E' = 55.8 \) and \( E'' = 14.2 \) kcal/mole. The smaller of the quantities \( E' \) and \( E'' \), which determines the rate of reaction, is \( E'' = 14.2 \) kcal/mole. Since \( E'' \) is positive, reaction should proceed readily.

According to Cottrell \cite{1}, "the determination of the exact value of the heat of formation of organic peroxides meets with great difficulties". The value of \( Q_{\text{O-O}} \) is therefore not known very accurately.
us examine the effect of the possible error in QO-O on the above result, for which purpose we shall regard QO-O as a variable in Equations (2) and (3). It will be seen from Equation (3) that \( E' \) does not depend on QO-O because the latter does not occur in the equation. The value of \( E' \), which is constant at 14.2 kcal/mole under the given conditions, will determine the rate of reaction until \( E' \) becomes equal to \( E' \). Substituting \( E' = 14.2 \) and the same values of \( Q \) (apart from QO-O) as before in Equation (2), we find that the limiting value of QO-O is 88.6 kcal. This limit exceeds the accepted value of 47 kcal by more than 40 kcal, which is certainly very many times the possible experimental error in the determination of QO-O. Hence, no probable error in the determination of QO-O can affect our conclusion, namely, that hydrogenolysis of the peroxide bond should proceed readily over nickel.

The above calculation concerns the mean O-O bond energy. As we have shown [4], substituents on O must affect \( E' \) and the rate of hydrogenolysis. However, until the individual RO-Ni and RO-H bond energies are known in their relation to the nature of the substituent R- as is required for the determination of \( E' \) from Equation (3) such calculations cannot be carried out. The position is just the same for future calculations from Equations (2) and (3) for other catalysts (K), because the C-K, O-K, and H-K bond energies are not yet known. From these examples the importance of determining bond energies concerned in catalytic processes will be seen. At the present only direct experiment can be taken as a basis in such matters.

There has been very little experimental study of the catalytic reduction of organic peroxides. There are only two or three references in the literature to the hydrogenation of peroxide compounds. Paget [5] found that over a palladium catalyst ascaridole is hydrogenated to an unsaturated menthenediol, whereas over a platinum catalyst the double bond is hydrogenated with formation of dihydroascaridole:

\[
\begin{align*}
\text{Ascaridole} & \xrightarrow{\text{Pd}} \text{Menthenediol} \\
\text{Ascaridole} & \xrightarrow{\text{Pt}} \text{Dihydroascaridole}
\end{align*}
\]

Dufraisse and Houillart [6] showed that in presence of Raney nickel photo-oxides of the anthracene and tetracene series are hydrogenated to the corresponding diols. It is indicated in a patent [7] that the hydrogenation of aromatic hydroperoxides can be effected over Raney nickel and cobalt catalysts under a pressure of 20-25 atm. The corresponding alcohols are obtained; for example, \( \alpha, \alpha\text{-dimethylbenzyl hydroperoxide} \) (cumene hydroperoxide) gives \( \alpha, \alpha\text{-dimethylbenzyl alcohol} \).

There has been no previous investigation into the kinetics of the hydrogenation of peroxides and hydroperoxides. The present paper gives experimental data on the hydrogenation of \( \alpha, \alpha\text{-dimethylbenzyl hydroperoxide} \) (I), \( \alpha, \alpha\text{-dimethylbenzyl ethyl peroxide} \) (II), 1, 2, 3, 4-tetrahydro-1-naphthyl hydroperoxide (III), and \( \text{di-tert-butyl peroxide} \) (IV) over Raney nickel and palladium black.

\[
\begin{align*}
\text{(I)} & \quad \text{(II)} & \quad \text{(III)} & \quad \text{(IV)} \\
\text{CH}_3\text{-C-O-OH} & \quad \text{CH}_3\text{-C-O-O-C}_2\text{H}_5 & \quad \text{O-OH} & \quad \text{CH}_3\text{-C-O-O-C}_2\text{H}_5 \\
\text{CH}_3\text{-C-O-OH} & \quad \text{CH}_3\text{-C-O-O-C}_2\text{H}_5 & \quad \text{O-OH} & \quad \text{CH}_3\text{-C-O-O-C}_2\text{H}_5
\end{align*}
\]

We obtained data on the rate of hydrogenation of the peroxide group and the effects of various factors on the course of this process. The experiments showed that in presence of Raney nickel the peroxide compounds (I) - (III) are already hydrogenated at \( E' \) under normal pressure. Under these conditions the consumption of hydrogen corresponds to hydrogenation of the peroxide to the alcohol. It was shown by the qualitative reaction with thiocyanate [8] that peroxide compounds were absent from the reaction products.