Electroreduction of isophthalaldehyde: An example of simultaneous reduction of two identical electroactive centers

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The diprotated form of isophthalaldehyde is reduced by two electrons to a diradical which, reduced further by two electrons, reacts with two protons to form a dialcohol. The stability of the diradical is much lower than that observed for ortho- and terephthalaldehydes. In acidic media isophthalaldehyde thus behaves like a simple benzaldehyde at twice the concentration. This course of the electrode process, based on polarographic reduction, has been confirmed by cyclic voltammetry and controlled potential electrolysis using a dropping mercury electrode. The diprotated molecules of isophthalaldehyde are oriented during the reduction process by such a way that probability of the electron transfer is the same for both groups. In the single protonated form of isophthalaldehyde, the group protonated at the electrode is reduced in a two-electron process to alcohol. The reduction of the second carbonyl group occurs at more negative potentials. At the time of reduction the molecule is oriented with one CH=OH group towards the surface. Investigation of the reduction of the unprotonated form is limited by the reaction of the dicarboxyaldehyde with hydroxide ions. Additions of hydroxide ions to carbonyl groups result in geminal dialcohols which are oxidized in alkaline solutions in two consecutive two-electron steps. One of the CH(OH)O groups is then oriented preferentially at the electrode surface. In isophthalaldehyde dioxime both protonated oxime groupings are reduced simultaneously in a single, eight-electron step.

The reduction of organic compounds bearing two identical electroactive groupings can occur either in two consecutive steps or simultaneously, in a single step. Consecutive reductions are observed for straight-chain compounds, in which two electroactive groups are separated by several sp² carbons. An example of such a process is the reduction of N,N-polyethylenem-bis-sydrones, where two reducible rings are separated by two or four methylene groups. Similar consecutive processes have been reported for reductions of some aromatic compounds, like polydioalthalates. For consecutive reductions it is necessary to assume that the investigated compound is oriented at the electrode surface in such a way that only one of the electroactive groups is in a sufficient distance from the electrode surface for the electron transfer to occur. Alternatively, such consecutive processes are observed for processes where an irreversible electron transfer is preceded by a chemical reaction (e.g. protonation) where such heterogeneous chemical reaction is facilitated by the orientation of the reactants at the electrode surface. For the first step in consecutive reductions the second group acts as a substituent. As reducible groups are usually electron-withdrawing, the presence of the second group results in a shift of the first reduction process to more positive potentials. Facilitation of the reduction of the first group was observed, for example, for some dinitrobenzenes.

When two identical electroactive groups are either in a vicinal position in aliphatic or alicyclic compounds or in ortho- or para- position on an aromatic ring, mutual interaction of the two groups can be very strong. The reduction pattern in such compounds is then different from that observed for analogous molecule with a single electroactive group. For example the electrochemical behavior of p-diacylbenzene differs principally from that of acetophenone and terephthaldehyde from that of benzaldehyde.

Observation of a simultaneous reduction of two electroactive centers in a single step indicates that the probability of both the electron and proton transfers is the same for both electroactive groups. That is possible when the compound is oriented at the electrode surface so that both electroactive groups are in a similar distance from the electrode surface.

The number of examples of simultaneous reduction of two identical groups reported in the literature is relatively limited. Such behavior has been observed, for example, for the reduction of some polynitrobenzenes in acidic media. The reduction of isophthalaldehyde in acidic media is another example of such system, in which not only electron transfers, but also...
the chemical reaction accompanying such transfer for the compound bearing two formyl groups is similar to benzaldehydes, bearing only a single formyl group.

Electrochemical reduction of isophthalaldehyde has so far received only limited attention. Its reduction in DMSO was briefly mentioned. In aqueous solutions it has been observed that current-voltage curves of this 1,3-dicarboxaldehyde differ principally from those of the 1,2- and the 1,4-dicarboxaldehydes. The difference has been attributed to the lack of stability of the biradical formed and the absence of hydration in the 1,3-isomer.

Materials and Methods

Instrumentation

Current-voltage curves were recorded for d.c. and differential pulse polarographic experiments using PAR Model 172 Polarographic Analyzer (Princeton Applied Research, Princeton, NJ) in connection with a Hewlett-Packard 7004B X-Y recorder. The capillary electrode for polarographic experiments had the following characteristics: \( m = 2.5 \text{ mgs}^{-1}, t = 3.2 \text{ s at } h = 60 \text{ cm at } 0.0 \text{ V (SCE)} \).

Cyclic voltammetry was carried out using an in house built instrument. Controlled potential electrolysis with a dropping mercury electrode was performed using the Cambridge Polarographic Analyzer 82P (Cambridge, U.K.) and preparative electrolysis with a mercury-pool electrode was carried out using a Bipolar Potentiostat Model 100-A (MI Associates, Cambridge, MA).

A Corning Digital 112 Research and Sargent Model DR pH-meters with a glass electrode were employed for pH-measurements of buffers.

For recording of current-voltage curves an electrolytic cell with calomel reference electrode separated by liquid junction (Kalousek cell) was used. For controlled potential electrolysis with DME a micro H-type cell was used in which 1 ml of the electrolysed solution was placed.

A Unicam SP-800-A (Pye-Unicam, Cambridge, U.K.) with temperature control of quartz cells was used for recording of UV-vis spectra.

A various Aerograph series 1200 Gas Chromatograph with a flame ionization detector was used for the analysis of purity of commercial aldehyde samples and product identification.

Chemicals and solutions

Isophthalaldehyde, benzaldehyde and tolualdehyde were supplied by Aldrich Company (Milwaukee, WI). Purity was checked by m.p., b.p. and glc of an ether solution of the aldehydes. Chemicals for preparation of buffers were of analytical quality.

Stock solution of aldehydes (0.01M) were prepared in acetonitrile or in absolute ethanol and stored in dark at 4°C. For initial studies Britton-Robinson buffers and for definite pH values simple phosphate, acetate, BICINE and borate buffers were used.

Procedure

For electrochemical studies 9.8 ml of the buffer containing 10% acetonitrile were deaerated by a stream of nitrogen. After addition of 0.2 ml of the 0.01M stock solution of the aldehyde in acetonitrile and brief introduction of nitrogen, the current-voltage curves were recorded at 25°C. Hence the final concentrations were \( 2 \times 10^{-4} \text{ M} \) aldehyde. Alternatively, in initial experiments buffers containing 30% acetonitrile or 2% or 52% ethanol were used.

For spectrophotometric measurements 0.1 ml of the 0.01M stock solution of the aldehyde was added to 9.9 ml of the buffer solution. Spectra were then recorded in the presence of air oxygen in solutions containing \( 1 \times 10^{-4} \text{ M} \) aldehyde and 1% ethanol.

Results and Discussion

Polarographic reduction

Initial experiments were carried out in buffered solutions containing 2% ethanol and \( 2 \times 10^{-4} \text{ M} \) isophthalaldehyde. Under such conditions polarographic i-E curves were strongly affected by adsorption. The effect of the adsorption was still marked when in such media the concentration of I was decreased to \( 5 \times 10^{-5} \text{ M} \). Increase in content of organic co-solvent to 52% (v/v) ethanol or 30% (v/v) acetonitrile eliminated complications due to adsorption, but even after correction for the change in viscosity the current-voltage curves manifested complicating solute-solvent interactions. These were attributed to changes in solvation of the electroactive species and to the effects on rates accompanying the electron transfer. Hence the most straight forward information about the course of the reduction was obtained in buffered solutions containing 10% (v/v) acetonitrile. In such solvent mixtures water was still the predominating solvating agent. All results described below were obtained in such solvent mixture. As boric acid interacts with the electroactive species, data reported for pH 8 to 10 were then obtained in a BICINE buffer.
The reduction of the dialdehyde I takes place in five waves, denoted here as \(i_{1A}, i_{1B}, i_{2A}, i_{2B}, \) and \(i_3\).

In acidic media, the reduction resembles closely that of aryl monocarbonyl compounds at twice as high concentration than that of the dialdehyde I. At pH<4 the reduction takes place in a two-electron wave \(i_{1A}\), the potential of which is shifted to more negative values with increasing pH (Fig. 2). At pH<2 the slope of the \(E_{1/2}-pH\) plot is 0.04V/pH, at pH 2 to 5 the slope is 0.055V/pH and the half-wave potential becomes pH-independent at pH>5 (Fig. 2). At pH>4 this wave \(i_{1A}\) is accompanied by another two-electron wave \(i_{1B}\) the half-wave potential of which is pH-independent. At pH<4 this wave is superimposed by the reduction current of hydrogen ions from the supporting electrolyte.

At pH greater than about 5.7 waves \(i_{1A}\) and \(i_{1B}\) are replaced by two-electron waves \(i_{2A}\) and \(i_{2B}\). Their limiting current remains constant up to pH 10. At pH>10 the heights of both of these waves decrease with increase in pH. Both plots of \(i_{2A}\) and \(i_{2B}\) as a function of pH have a shape of a decreasing dissociation curve with an inflection point (pK') at a pH about 10.6 for wave \(i_{2A}\) and about 11.5 for wave \(i_{2B}\) (Fig. 1). The slopes of \(E_{1/2}-pH\) plots for wave \(i_{2A}\) were 0.065V/pH at pH 6 to 7 and 0.045V/pH at pH 7 to 10. At pH>10 the half-wave potential of wave \(i_{2A}\) becomes pH-independent. For the wave \(i_{2B}\) the slopes \(dE_{1/2}/dpH\) were 0.050V/pH between pH 6 and 10 and the half-wave potential of wave \(i_{2B}\) becomes pH independent at pH>10.

At pH>10.6 the half-wave potential of wave \(i_{2B}\) becomes pH-independent (Fig. 2), as expected for a reduction preceded by a protonation.

Finally, at pH between 11 and 12 the wave \(i_3\) at more negative potentials was observed. Its height also decreased with increase in pH (Fig. 1).

The dependences of limiting currents and half-wave potentials on pH can be interpreted by Scheme 1.

For waves \(i_{1A}\) and \(i_{1B}\) the experimental evidence indicates the presence of processes (1)-(4):

\[
\begin{align*}
\text{Ar(CHO)}_2 + 2H^+ \rightarrow \text{Ar(CHOH)}_2^+ \quad \text{(1)} \\
\text{Ar(CHOH)}_2^+ + 2e^- \rightarrow \text{Ar(CHOH)}_2 \quad \text{(2)} \\
\text{Ar(CHOH)}_2 + 2e^- \rightarrow \text{Ar(C HOH)}_2 \quad \text{(3)} \\
\text{Ar(C HOH)}_2 + 2H^+ \rightarrow \text{Ar(CH}_2\text{OH)}_2 \quad \text{(4)}
\end{align*}
\]

Scheme 1

Ratio of limiting currents \(i_{2A} : i_{2B}\) is close to 1.0. This indicates that dimerization of the diradical formed in reaction (2) does not play an important role under conditions used. The lifetime of the diradical for I is, nevertheless, much shorter than those observed for benzene 1,2- and 1,4-dicarboxaldehydes, as manifested by the absence of anodic processes on curves obtained by cyclic voltammetry.

In the medium pH-range, between pH 5.7 and 10 the reduction of the dialdehyde I does not correspond.
to a simultaneous reduction of both aldehydic groups.

For simple benzylic aldehydes or acetophenones\(^9\) in this pH range a single two-electron wave is observed, the half-wave potential of which is in most cases pH-independent. It is attributed, based on behavior of higher pH values, to a sequence e, H\(^+\), e, H\(^+\). In first two steps of this sequence a radical anion formed is rapidly protonated. The resulting radical is rapidly further reduced to alcohol. Hence a single two-electron wave is observed as long as the rate of protonation is sufficient to convert all the radical anion into an easily reducible radical.

Comparison of the half-wave potential of the second wave of I (i\(_{2B}\)) with half-wave potentials of 3-tolualdehyde indicated that in this range in waves i\(_{2A}\) and i\(_{2B}\) a consecutive reduction of the two aldehydic groups occurs. The presence of the second formyl group, acting as a substituent, not only facilitates the reduction and results in a shift of wave i\(_{1A}\) to a more positive potential, but also facilitates the surface protonation of the formyl groups. This is reflected by pH-dependence of the half-wave potential of wave i\(_{2A}\). Hence the process in wave i\(_{2A}\) can be depicted as given in Eqs (5) and (6).

\[
\text{Ar(CHO)HCHO} + \text{H}^+ \xrightarrow{\text{surface}} \text{Ar(CHOHCHO)} \quad \text{(5)}
\]

\[
\text{Ar(CH\(_2\)OHCHO} + 2e + \text{H}^+ \xrightarrow{\text{Ar(CH\(_2\)OHCHO}} \quad \text{(6)}
\]

In wave i\(_{2B}\), thus, the substituted benzylic aldehyde Ar(CHOHCHO) is reduced. At pH>10 even the surface protonation of Ar(CHOH) in (5) is not rapid enough to convert all the dialdehyde into a monoprotonated species according to (5). This results at pH above 10 in a decrease of i\(_{2A}\) and i\(_{2B}\) with increase in pH (Fig. 1). These waves are gradually replaced by wave i\(_{3}\) at more negative potentials (Fig. 2). The negative value of the half-wave potential of wave i\(_{3}\) as well as its dependence of pH (Fig. 2) indicate a reduction of an unprotonated species (7):

\[
\text{Ar(CHO)} + e \xrightarrow{\text{Ar(CHO)}(\text{CHO})^-} \quad \text{(7)}
\]

The fate of the radical anion and distinction between a mono and diradical is prevented by a bulk chemical reaction. At pH>11 addition of hydroxide ions to the aldehyde I takes place in reactions (8a and b):

\[
\text{Ar(CHO)} + \text{OH} \xrightarrow{\text{Ar(CHO)(OH)O^-}} \quad \text{(8a)}
\]

\[
\text{Ar(CHO)(OH)O} + \text{OH} \xrightarrow{\text{Ar(CHO)(OH)O^-}} \quad \text{(8b)}
\]

The resulting geminal diol anion is electroactive and its formation results in a decrease of wave i\(_{3}\) with increasing activity of hydroxide ions.

Limiting currents i\(_{1A}\) and i\(_{1B}\), similarly as currents i\(_{2A}\) and i\(_{2B}\) in the pH region where they are pH-independent, are diffusion controlled as shown by the linear dependence on the square root of mercury pressure. Whereas the reductions of benzene 1,2- and 1,4-dicarboxaldehydes in the presence of 52% ethanol indicate nucleophilic addition of the alcohol to formyl groups, no such effect of ethanol has been observed for the studied 1,3-dialdehyde I.

Spectroscopic data indicate that nucleophilic addition of hydroxide ions occur in consecutive rather than simultaneous processes (8a, 8b). Attack of one hydroxide ion on the dicarboxaldehyde I at a time is in agreement with the pattern of electrooxidation (see below), where the oxidation of two formyl groups occurs in consecutive processes, both involving addition of OH- groups prior to electron transfers.

**Cyclic voltammetry (CV)**

The absence of anodic peaks on cyclic voltammograms at pH between 2 and 12 at scan rates up to 500 mV/s indicated irreversibility of processes in waves i\(_{pl}\) and i\(_{p2}\). Otherwise CV did not offer additional information about the processes involved than DC polarography. The pH-dependsence of peak currents of i\(_{pl}\) and i\(_{p2}\) as well as those of peak potentials resembled that obtained with a higher accuracy in DC polarography. In particular, peaks i\(_{pl}\) and i\(_{p2}\) practically overlap, similarly as peaks i\(_{2A}\) and i\(_{2B}\) at pH>8.

**Controlled potential electrolysis (CPE)**

To obtain information comparable to that obtained by DC polarography, the CPE was carried out in 1 ml of a 1x10 \(^{-4}\) M solution of isophthalaldehyde (1) containing 10% v/v ethanol to increase the solubility. The electrolysis was carried out in a semimicrowell, where the solution was stirred by the falling off mercury drops, using the dropping mercury electrode. Typical experiments were carried out in the absence of oxygen for a period of about 7 to 8 hours, which resulted in a 70 to 80% conversion.

The electrolysis at pH 2 at the limiting current of wave i\(_{1A}\) yielded a straight plot of log\(_{10}\) i\(_{1A}\) = f(t) with a
slope corresponding to a two-electron process. Wave 

\[ i_{1/2} \]  

is at this pH overlapped by the current of hydrogen evolution. The time dependence of wave \[ i_{1A} \] resembled closely the decrease in absorbance at 230 nm in the UV spectrum. The product was identified as a pinacol using gas chromatography, a dimer formed by interaction of two electrogenerated radicals, involving some hydrogen abstraction from the solvent.

Electrolysis in a phosphate buffer of pH 6.8 containing 10% v/v ethanol at a potential corresponding to the limiting current of wave \[ i_{2B} \] resulted in a linear plot of \( \log(i_{2A}+i_{2B}) = f(t) \) with a slope corresponding to a transfer of four electrons. No new wave appeared during the electrolysis. In the course of electrolysis the absorbance at 230 nm decreased with time similarly as the decrease in \( i_{2A} \). The decrease was accompanied by an increase in a low-intensity band at 250 nm. The electrolysis product was identified as dialcohol, Ar(CH$_2$OH)$_2$ using gas chromatography.

The electrolysis at pH 10 at the limiting current of wave \( i_{2A} \) was carried out in a borate buffer which could have resulted in some of the observed complications. A clearer picture has been observed at \( t<4h \), where the decrease in wave \( i_{2A} \) was accompanied by an increase in wave \( i_{2B} \). At longer times the height of \( i_{2B} \) remained constant, but the height of wave \( i_3 \) decreased (Fig. 3). No further attention has been paid to the behavior at \( t>4h \). In the course of electrolysis the \( \Pi \rightarrow \Pi^* \) band at 230 nm decreased and the time dependence was analogous to the decrease of \( i_{2A} \). The weaker benzenoid band at 250 nm also somewhat decreased. This behavior is consistent with the above interpretation that in \( i_{2A} \) protonated form of one of the aldehydic groups is reduced.

At pH>11 investigation of the electrolysis was complicated by homogeneous reaction, involving hydroxide ions, observed also in the absence of applied potential.

**Anodic oxidation**

Similarly as for the other substituted benzaldehydes, isophthalaldehyde (I) yields in alkaline solutions containing 2% v/v ethanol anodic polarographic waves corresponding to the oxidation of geminal diol anions (grouping =CH(OH)O). In 1.0 M and more concentrated solutions of sodium hydroxide, the oxidation took place in two anodic waves (\( i_A \) and \( i_B \)) of equal height, separated by about 0.1 V. At lower pH values than about 12 these waves were gradually superimposed by the current of anodic dissolution of mercury. Comparison of the total anodic current (\( i_A + i_B \)) with anodic limiting currents of some monosubstituted benzaldehydes (Table 1) indicated that the current (\( i_A + i_B \)) for the dialdehyde was twice that observed for the two-electron oxidation of monocarboxaldehyde. The half-wave potentials of both anodic waves (\( i_A, i_B \) of the dialdehyde I were shifted with increase in pH to more negative values by about 0.13V/pH.

As the DC polarographic curves were difficult to measure, the differential pulse polarography was applied. Peak currents \( i_{pA} \) and \( i_{pB} \) corrected for changes in viscosity were independent of basicity from pH 13 to 14.5. In solutions in 0.5M to 0.005M NaOH at constant ionic strength (\( \mu=0.5 \)) the anodic peak currents...
for both peaks decrease with decrease in concentration of sodium hydroxide. The plot of the decrease in peak current $\Delta i_{pA}$ of the more positive wave with decrease in pH has a shape of a dibasic dissociation curve (Fig. 4). The measurements of $\Delta i_{pA}$ were not sufficiently accurate to conclude with certainty that the observed decrease with decrease in pH corresponds to a monobasic acid.

The anodic process involved in wave $i_A$ can be thus depicted by Eqs (8a)-(9).

$$\text{Ar(CHO)}_2 + \text{OH} \longrightarrow \text{Ar(CHO)[CH(OH)O]} \quad \ldots \ (8a)$$

$$\text{Ar(CHO)[CH(OH)O]} \rightarrow \text{Ar(CHO)COO} + 2\text{H}^+ + 2\text{e}^- \quad \ldots \ (9)$$

whereas in wave $i_B$ the processes are (10) and (11):

$$\text{Ar(CHO)COO} + \text{OH} \longrightarrow \text{Ar[CH(OH)O]} \quad \ldots \ (10)$$

$$\text{Ar[CH(OH)O]} \rightarrow \text{Ar[COO]}_2 \quad +2\text{H}^+ + 2\text{e}^- \quad \ldots \ (11)$$

From the decrease of anodic wave of I with decrease in pH, it is possible to calculate the rate constant for the addition of first hydroxide ion to isophthalaldehyde using Eq. (12).\(^{10}\)

$$\log k_1 = pK - 2pK' = pK_a - \log t_1 - 2\log(1.15) \quad \ldots \ (12)$$

where $K$ is the equilibrium constant of reaction (8a), $pK = \text{pH}$ where the anodic current reaches half of its diffusion controlled value, $K_a$ is the ionic product of water and $t_1$ is the drop-time. For experimentally found $pK=13.23$ and $pK=11.5$ and $t_1=3s$, $\log k_1$ value was obtained as 3.77, comparable to values obtained for substituted benzaldehydes.

Some chemical reactions of isophthalaldehyde (1)

Whereas terephthalaldehyde and in particular orthophthalaldehyde\(^{11,12}\) add water readily in aqueous solutions covalently, polarographic evidence indicates that isophthalaldehyde show in aqueous solutions negligible tendency to add covalently water, similar to majority of substituted benzaldehydes.

In 1M and more concentrated solutions a slow, consecutive reaction results in an increase in the absorbance at 280 nm. This might be a Cannizzaro reaction involving one of the formyl groups. The other aldehydic group remains and can undergo polargraphic reduction and formation of a 2,4-dinitrophenylhydrazone.

At pH between 4 and 5.7, where the sum of limiting currents $i_{iA}$ and $i_{iR}$ of isophthalaldehyde corresponds to a transfer of four electrons, an addition of hydroxylamine results in a shift of the half-wave potential by 50 to 100 mV, to more positive values than the reduction of the carbonyl groups in $i_{iA}$. To achieve completion of the reaction, the reaction mixture was kept at 25°C for 5 to 6 hours before recording of the

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Fig. 4—The dependence of peak current ($\Delta i_{max}$) of the anodic oxidation of $2\times10^{-3}M$ isophthalaldehyde on pH in solutions of sodium hydroxide containing 2% ethanol. Wave $i_A$ (●), $i_B$ (○). For the more positive wave $i_B$ is plotted a theoretical dissociation curve.

Fig. 5—Dependence of the limiting current of the reduction wave of the isophthalaldehyde dioxime on concentration of hydroxylamine. Acetate buffers pH 3.9 (●), 4.7 (○), 5.7 (△), contained initial concentrations of $2\times10^{-3}M$ isophthalaldehyde and 2% ethanol. Curves were recorded 5-6 hrs. after the addition of hydroxylamine.
current-voltage curves. The limiting current of the product increased with increase in concentration of hydroxylamine. A plot of the limiting current as a function of concentration of hydroxylamine shows two linear segments (Fig. 5). Their intersection, above which the current does not increase with increase in concentration of hydroxylamine, occurs at a concentration of hydroxylamine that is twice the initial concentration of the dialdehyde I. This indicates formation of a dioxime of the isophthalaldehyde, which, in this pH-range, is reduced in a single eight-electron step.

The slope of the plot of $i = f(NH_2OH)$ indicates that the equilibrium (13) between the dicarboxaldehyde and hydroxylamine is practically completed in favor of the dioxime, which prevents determination of the equilibrium constant of reaction (13):

$$\text{Ar(CHO)}_2 + 2\text{NH}_2\text{OH} \rightleftharpoons \text{Ar(CHOH)}_2 + 2\text{H}_2\text{O} \quad \ldots \quad (13)$$

A single eight-electron reduction of the dioxime of isophthalaldehyde indicates simultaneous reduction of both oxime groupings. Thus the orientation of the dioxime at the electrode surface must allow a comparable probability of electron and proton transfers to both oxime groups.

Conclusions

Electroanalytical studies, in particular of variations of limiting currents and half-wave potentials with pH, offer useful information about the orientation of organic molecules with two identical electroactive groups at the electrode surface during the reduction or oxidation. In investigated reductions of isophthalaldehyde the rate of surface protonation enables either a simultaneous reduction of both electroactive groups (in diprotonated species) or a consecutive one (in a monoprotonated isophthalaldehyde). In the digeminal diol anionic form, resulting in addition of hydroxide ion in alkaline solution, the oxidation occurs as a consecutive process. This study also indicates the importance of choice of solvent and of kind of buffer to obtain optimum (and simplest) conditions for a mechanistic study.

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References