

Use of a chemical reaction for mechano-optical signal transduction

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Abstract

A novel reaction system for generating optical response from a mechanical stimulus is reported. The reaction system exhibits an oscillatory optical response which can be regulated by means of an external mechanical variable. Color formation is initiated by mechanical perturbation while the system undergoes a transition to a colorless state in the absence of a mechanical stimulus. The unique mechanochromic characteristics of the redox reaction between the reduced form of β -nicotinamide adenine dinucleotide (NADH) and the oxidized form of the redox-active dye 2,6-dichlorophenolindophenol (DPIP) are utilized to translate a mechanical signal to an optical output for use as a simple solution-based mechano-optical signal transducer.

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1. Introduction

The ultimate of design of molecularly-designed functional device elements, at present, necessitates evaluation of novel signal transduction strategies based on molecular components [1–3]. For design of signal-transducing elements, functional interconversion of an input to suitable response is a vital criterion [4]. In its simplest form, a signal-transducing system must be capable of existing in two different states, which can be interconverted by means of a suitable signal [5]. If there are associated optical or electronic changes then such a system provides an ideal approach to design of signal-transducing elements [6,7]. Primarily, signal transduction can be achieved by means of a bistable system, wherein the two states of the system can be interchanged by application of an external stimulus and the measurable physicochemical differences between the two states serve as a response.

Herein, we demonstrate the feasibility of a strategy for transduction of a mechanical signal (or input) to an optical response (or output) by using an oscillatory reaction system that responds to external mechanical perturbations by undergoing a transition from a colorless to a colored state. The reaction system exhibits an optical response which can be regulated by means of an external mechanical variable. Color formation is initiated by a mechanical perturbation while the system undergoes a transition to a colorless

state in the absence of a mechanical stimulus. The unique mechanochromic characteristics can be exploited for the design of a novel mechano-optical signal transducer.

2. Experimental

2.1. Chemicals

β -Nicotinamide adenine dinucleotide (NADH, reduced form) was purchased from Sigma Chemical Co. (St. Louis, MO, USA) and 2,6-dichlorophenolindophenol (DPIP) sodium salt hydrate was purchased from Acros Organics (Pittsburgh, PA, USA).

2.2. Design of mechanochromic reaction system

2.2.1. Sample preparation

The reaction mixture studied comprised of 10.2 mg (14.4 μ mol) of β -NADH and 0.3 mg (1.6 μ mol) of sodium salt of DPIP dissolved in 0.4 ml of deionized water. This mixture has a blue color, which fades away and the solution turns clear in less than 10 min. The solution was immersed in a 1 mm \times 10 mm cuvette that served as container. The cuvette was covered with parafilm such that a bubble of air on top was trapped inside the cuvette.

2.2.2. Optical measurements

Optical characterization of the materials was done using absorbance measurements. Absorption spectra were taken

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with a UV-Vis Hewlett-Packard model 8453 spectrophotometer. The kinetic mode was used to monitor the intensity variations.

2.3. Evaluation of mechano-optical response

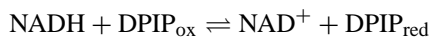
The reaction mixture consisted of 10.2 mg (14.4 μmol) of NADH, and 0.3 mg (1.6 μmol) of sodium salt of DPIP dissolved in 0.4 ml of deionized water. The reaction was studied by mixing NADH and sodium salt of DPIP in water. Upon mixing the reactants, the original blue color of DPIP slowly fades and the solution turns clear in ~ 10 min. Optical measurements of this reaction were performed by using a quartz cuvette with 1 mm optical path. The cuvette was filled with 0.4 ml of the reaction mixture and sealed with parafilm. This leaves a small air-bubble at the top of the cuvette that can be used to monitor the number of mechanical rocking cycles. The optical absorption spectra and time profiles of absorbance variations were recorded using HP 8453 spectrophotometer. The coloration–decoloration cycles were obtained by recording spectra at intervals of 60 s. For monitoring the effects of mechanical stimulus, the cuvette was removed from the sample holder and was subjected to rocking undulations for 45 s prior to recording the spectrum. The rate of mechanical rocking was kept constant at one rocking cycle per 5 s. The absorption changes of the solution during the treatment were monitored in a kinetic mode set to take one spectrum every minute.

3. Results and discussion

3.1. Design strategy for mechano-optical signal transduction

When a chemical reaction allows for an external feedback [8], it provides unique opportunities that are not possible with a self-sustaining reaction occurring under a thermodynamically closed set of conditions. By definition, a thermodynamically open reaction systems exhibit temporal changes in concentration of chemical constituents with respect to external physicochemical perturbations. If there is an associated measurable response then external feedback induced chemical oscillatory reactions can furnish an ideal set of characteristics that can be used for design of a signal-transducing system. For such a system an external control variable, feedback, and bistability are critical. A signal-transducing chemical system necessitates fulfillment of three particular requirements: (i) bistability which can be structural, optical, or electronic, (ii) an external stimulus or signal for interconversion between the two states, (iii) a measurable optical or electronic response arising due to a transition of the system from one state to another. Such a system can be used as a means for transduction of a signal from one form to another wherein the stimulus represents an input signal while the measured response constitutes the output.

The chemical reaction studied in this work is based on a spontaneous redox reaction between NADH and the oxidized form of DPIP. Overall, the reaction is given as



The oxidized form of DPIP is intensely blue colored ($\lambda_{\text{max}} = 615$ nm) while the reduced form is colorless. In order to make the reaction kinetics pseudo-first-order with respect to DPIP, an excess of NADH relative to DPIP is used. Under these conditions, the reaction is shifted towards the products and a colorless solution is obtained. A particularly remarkable feature observed with this reaction system is that it can undergo reversible changes in optical density at 615 nm with respect to mechanical perturbations. Thus, the colorless solution turns blue when the reaction container is perturbed by an external mechanical stimulus in the form of gentle rocking of the reaction container. The color increases in intensity until a saturation is reached. This colored solution returns to its original clear form when allowed to rest undisturbed. This coloration–decoloration cycle is reversible and can be repeated several times.

3.2. Evaluation of system response

The reaction was studied by mixing β -NADH and sodium salt of DPIP in water. The reaction mixture consisted of 10.2 mg (14.4 μmol) of NADH, and 0.3 mg (1.6 μmol) of sodium salt of DPIP dissolved in 0.4 ml of deionized water. Upon mixing the reactants, the original blue color of DPIP slowly fades and the solution turns clear in ~ 10 min. Optical measurements of this reaction were performed by using a quartz cuvette with a 1 mm optical path. The cuvette was filled with 0.4 ml of the reaction mixture and sealed with parafilm. This leaves a small air-bubble at the top of the cuvette which can be used to monitor the number of mechanical rocking cycles. The coloration–decoloration cycles were obtained by recording spectra at intervals of 60 s. For monitoring the effects of mechanical stimulus, the cuvette was removed from the sample holder and was subjected to rocking undulations for 45 s prior to recording the spectrum.

The optical response of the reaction was monitored at 615 nm as shown in Fig. 1. The original clear solution turns blue and the absorbance increases with respect to rocking of the cuvette. When the system is left undisturbed, the absorbance drops and the solution becomes colorless. As shown in Fig. 1, the increase in intensity is due to mechanical perturbation of the system while the decrease in intensity takes place when the system is at rest. The plot of intensity at 615 nm represents changes in concentration of the oxidized form of DPIP. Thus, mechanical rocking of the cuvette results in an increase in concentration of DPIP_{ox} . When the system is allowed to rest, a slow decay of DPIP_{ox} peak is observed indicating depletion of DPIP_{ox} concentration. A distinctive feature of this oscillatory reaction system is that the periodic changes in concentration of DPIP are induced by mechanical factors. The data indicates that the

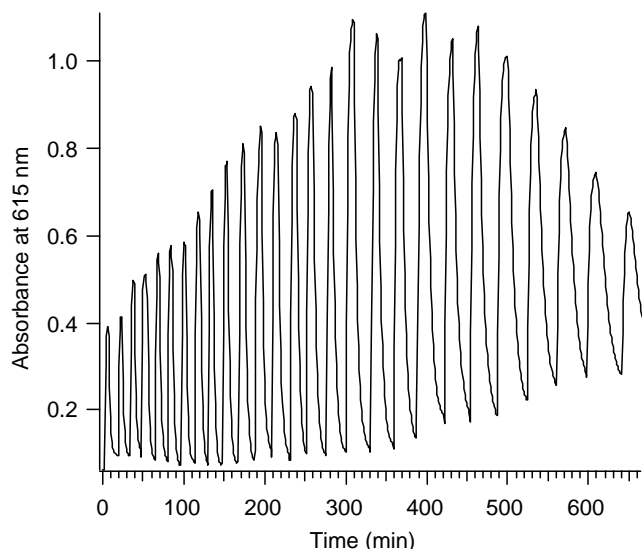


Fig. 1. Time profile of absorption intensity variation at 615 nm for the NADH–DPIP reaction system showing the oscillatory mechanochromic response. The absorption spectra were obtained at intervals of 60 s. The increase in intensity is associated with mechanical rocking of the cuvette while the decrease in intensity occurs when the cuvette is left undisturbed.

coloration–decoloration steps are dependent on the overall state of the system, and the application of mechanical stimulus leads to temporal variations in concentrations of the chemical constituents.

Mechanical rocking of the cuvette containing the reaction mixture results in generation of DPIP_{ox} as shown by the formation of an intense peak centered at 615 nm in the optical spectra (Fig. 2, inset). The movement of air-bubble

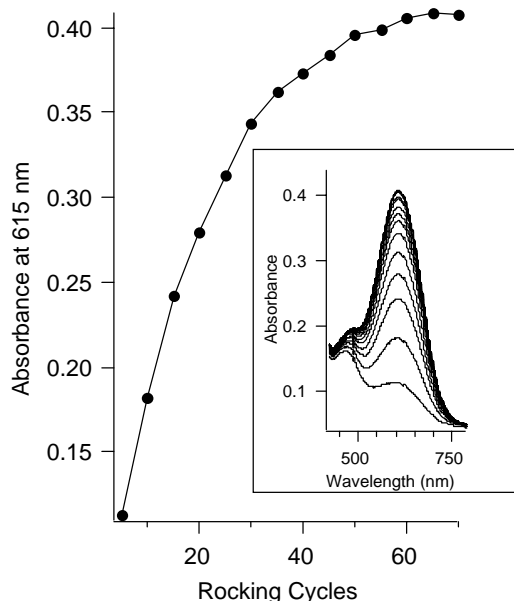


Fig. 2. Mechano-optical correlation curve for the optical density at 615 nm with respect to the number of rocking cycles. Inset shows the optical absorption spectra for the data showing the increase in absorbance of NADH–DPIP reaction system.

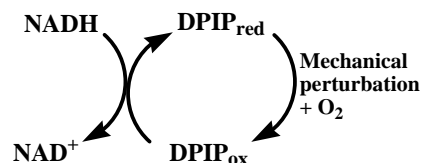


Fig. 3. Schematic depiction of the molecular mechanism of mechano-optical signal transduction.

from top to bottom and back to top of the cuvette as a result of rocking was taken as one cycle, which represents a unit mechanical variable. The increase in intensity of the 615 nm peak directly correlates with the number of rocking cycles. The results for a typical correlation between the number of rocking cycles and optical density are shown in Fig. 2. The response is linear initially and shows a saturation as the number of rocking cycles increases. The correlation can be used to measure the extent of an applied mechanical stimulus.

Although at present a detailed understanding of the reaction mechanism and kinetics remains to be established, the current results indicate that mechanical rocking of the cuvette with an air-bubble trapped inside leads to generation of the oxidized form of DPIP (this is consistent with the observation that oxidation of DPIP is not observed when the reaction is carried out under nitrogen). This indicates air-oxidation of DPIP_{red} which is known to undergo rapid oxidation in the presence of air [9]. Based on this, the overall putative mechanism of the reaction is depicted in Fig. 3. Initial mixing of NADH and DPIP_{ox} results in reduction of DPIP_{ox} due to electron-transfer from NADH, and the solution becomes colorless. Mechanical mixing of the solution results in air-oxidation of DPIP_{red} with the formation of blue color. Evidently the electron-transfer reaction between NADH and DPIP_{ox} is a slow process that allows a buildup of DPIP_{ox} under the conditions of an applied mechanical stimulus in the presence of oxygen. The reaction system is now in the so-called “far-from-equilibrium” state. When the system is kept at rest, DPIP_{ox} is reduced by the excess NADH as indicated by decoloration of the reaction mixture. This cycle of decoloration followed by mechanically induced coloration can be repeated as long as there is an excess NADH present within the system. However, in the long-term, a convergent decay of the optical response is observed due to depletion of NADH accompanied by an irreversible loss of the signal–response behavior.

This mechanism is supported by the observed trend in the intensity of DPIP_{ox} absorption at 615 nm during the coloration–decoloration cycles (Fig. 1). The intensity maxima during the color-forming step increase gradually with every cycle reaching an optimum value at ~ 300 min. Thereafter, subsequent cycles result in a gradual decrease indicating that total recovery of DPIP_{ox} is prevented. On the other hand, the residual intensity minima associated with the decoloration step are more or less constant until

~300 min followed by a gradual increase. These features suggest dynamic temporal variations in concentration of DPIP and a direct feedback mechanism associated with externally applied mechanical stimulus. Initially when there is a large molar excess of NADH, the air-oxidation of DPIP_{red} is counteracted by reduction with NADH and the accumulated concentration of DPIP_{ox} is not very large. Subsequent cycles deplete the concentration of NADH and therefore a large transient buildup of air-oxidized DPIP as a result of mechanical rocking is feasible. However, as the excess concentration of NADH decreases, the system reaches more towards an equilibrium state. The overall steady-state concentration of DPIP_{red} is less (i.e. DPIP_{ox} predominates) under these conditions as the reaction is shifted towards the reactants. The increased residual concentration of DPIP_{ox} is evident in the gradual enhancement of intensity minima as more cycles are performed after ~300 min. The intensity maxima for the coloration cycles show a continuous decrease due to the fact that the overall concentration of DPIP_{red} is diminished in the system and therefore only smaller amounts of DPIP_{ox} can be generated due to air-oxidation. Thus, overall the observed trend of an initial increase of peaks, a gradual increase of background minima in later part, broadening of the peaks (Fig. 1), and saturation of response (Fig. 2) is due to depletion of available oxygen along with shift of equilibrium towards a steady-state.

4. Conclusions

In conclusion, a novel mechano-optical signal-transducing system based on a chemical reaction wherein the oscillations can be introduced by mechanical perturbation of the reaction is reported in this work. The reaction exhibits the unique property of showing external mechanical stimulus regulated feedback. Mechanical rocking of the reaction mixture leads to coloration while a decoloration is observed in the absence of a mechanical stimulus. The air-oxidation of DPIP with mechanical mixing of the solution provides a positive feedback while the slow reduction of DPIP by NADH constitutes a negative feedback for the optical response. The mechanochromic system can be used to translate a mechanical signal to an optical response, and

therefore, illustrates a novel example of a simple easy-to-use mechano-optical signal transducer.

Acknowledgements

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Biographies

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