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Klok, Martin; Browne, Wesley R.; Feringa, Ben L.

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Kinetic analysis of the rotation rate of light-driven unidirectional molecular motors

Martin Klok,^{ab} Wesley R. Browne^{ab} and Ben L. Feringa^{*ab}

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The combination of a photochemical and a thermal equilibrium in overcrowded alkenes, which is the basis for unidirectional rotation of light-driven molecular rotary motors, is analysed in relation to the actual average rotation rates of such structures. Experimental parameters such as temperature, concentration and irradiation intensity could be related directly to the effective rates of rotation that are achieved in solution by means of photochemical and thermal reaction rate theory. It is found that molecular properties, including absorption characteristics and photochemical quantum yields, are of less importance to the overall rate of rotation than the experimental parameters. This analysis holds considerable implications in the design of experimental conditions for functional molecular systems that will rely on high rates of rotation, and shows that average rotation rates comparable to ATPase or flagella motors are within reach assuming common experimental parameters.

Introduction

There is currently major interest in the development of dynamic molecular systems as key components in the development of functioning molecular nanomachinery.¹ Such “motor like” systems should comply with the presence of Brownian motion,² which cannot be avoided under realistic conditions of application. That this is possible is exemplified by biological systems, where dynamic functions operate even in biomolecular systems in ambient solution-like phases.³ Controlled translational⁴ or rotary⁵ motion of objects on a molecular scale is frequently observed in biology varying from muscle contraction to membrane and cellular transport to flagella movement and mitosis. Separately, the possibility of work being delivered by molecular systems has been well established.⁵ In order to reach dynamic functionality in artificial systems, the laws of interaction at low Reynolds number will have to be understood, and theoretical frameworks to adapt to such conditions have been developed.⁶ The control of molecular motion in itself is a first step, but achieving motion at high rates seems indispensable for nanomachinery to function. Many molecular motors and switches designed so far rely on photochemical processes for their functioning.^{1,7} Although photochemical processes are generally perceived as much faster than thermal processes, experimental parameters, including irradiation intensity, have a profound influence on a photochemical transformation, which may not be appreciated immediately. Although a single photochemical process is in general faster than a thermal process, the

availability of photons may render the overall rate of conversion of a photochemical process slower than that of a thermal process, especially in the case where thermal barriers are low.

Molecular processes can only be expected to have an influence on their surroundings if the processes (a) have high amplitude or (b) are fast enough to be able to distinguish them among and apart from Brownian motion. Molecular motors,^{7a,8} stirrers,⁹ and swimmers¹⁰ can only be expected to display functionality if their absolute rate of motion allows them to stand out from the Brownian environment. Light-driven unidirectional rotary motors rely for their function on a combination of photochemical and thermal equilibria, and the actual rotation rate is therefore defined by a balance of the overall photochemical rate of conversion and the thermal rate of conversion. For this reason, the development of potential rotation rates at MHz frequencies¹¹ requires an analysis of what rates of rotation are actually achieved given experimental parameters. In the present paper, a kinetic analysis of the rotational equilibrium of molecular motors is presented, with which the actual rate of rotation can be determined as a function of experimental variables. It holds important implications for molecular photochemical systems that in their dynamic function are dependent on high overall rates of motion.

Our ongoing program of the development of unidirectional light-driven molecular motors based on rotation around a carbon–carbon double bond that functions as the axle of rotation has placed considerable attention on acceleration of the process of rotation (Scheme 1).⁸ These overcrowded alkene-based structures display unidirectional rotary behaviour by virtue of a sequence of consecutive photochemical *cis*–*trans* isomerisation steps followed by thermal helix inversion steps (Fig. 1).

In the most stable form A, an overcrowded alkene-based molecular motor adopts a helical shape due to steric interactions between the stator and rotor units, with the

^a Laboratory of Organic Chemistry, Stratingh Institute for Chemistry and Center for Systems Chemistry, Zernike Institute for Advanced Materials, Groningen, 9747 AG, The Netherlands.
E-mail: b.l.feringa@rug.nl; Fax: +31 50 363 4278;
Tel: +31 50 363 4296

^b Faculty of Mathematics and Natural Sciences, University of Groningen Nijenborgh 4, Groningen, 9747 AG, The Netherlands

Scheme 1 Basic structure of a light-driven unidirectional molecular motor, in which the rotor rotates unidirectionally relative to the stator under the influence of light.

Fig. 1 General rotation cycle of high-speed molecular motors. A photochemical reaction of A results in higher energy species B, which thermally reverts to A' by a passing of the rotor upper half over the stator lower half. A subsequent pair of photochemical and thermal helix inversion steps complete the 360° rotary cycle.¹²

helicity being determined by the absolute configuration at the stereogenic centre. The stereogenic centre controls the helicity through the favoured (pseudo-)axial orientation of the methyl group at this position, in order to minimise steric repulsion with the stator. A photochemical *cis-trans* isomerisation results in the naphthalene rotor part settling on the other side of the double bond, which inverts its helicity (form B, B'). However, the substituent at the stereogenic centre is then positioned in a (pseudo-)equatorial orientation, with a concomitant increase in steric repulsion with the stator. This raises the ground state energy of B relative to A by typically 12–20 kJ mol⁻¹. A thermally activated helix inversion releases this strain (B to A') by orienting the substituent at the stereogenic centre again into the more favoured (pseudo-)axial orientation. The overall result of the photochemical and subsequent thermal step is the same compound, but with the rotor rotated 180° relative to the stator. In the case where R ≠ H, the stable (A, A') conformations of the molecule represent different isomers of the same compound; the same holds for the two less stable (B, B') conformations. The spectroscopic difference between the two stable, and two

unstable, states, introduced by a substituent R, is used to study the unidirectionality of the process, because substitution at the R-position renders the B to A conversions of each half of the cycle inequivalent. However, if R = H, the conformations depicted as A in Fig. 1 are equal, and the rotational equilibrium can be summarised according to Fig. 2.

Photochemical *cis-trans* isomerisation of alkenes, *e.g.* stilbenes, occurs within picoseconds after absorption of a photon.^{7b,13} Recently it was confirmed that this holds for alkene-based molecular motors as well.¹⁴ As a result it has been presumed that the thermal process is rate limiting to the overall rate of rotation. With the recent realisation of a system capable of a maximum rotation rate of up to 3 MHz in theory,¹¹ the question now arises as to what rotation rates are actually achievable in solution, given the intensity of light available. Since experimental imaging of continuous molecular rotation, especially at high rates, remains a challenge, a theoretical analysis of the overall rotation rate of a unidirectional molecular motor is presented here based on photochemical and thermal reaction rate theory.

Background

Despite the apparent simplicity of the unimolecular photochemical reaction A → B, its kinetic analysis presents considerable difficulty compared with the related unimolecular thermal reaction B → A due to the non-linear nature of light-matter interactions *via* the photokinetic factor, F .¹⁵ In 2007, a closed form integration of a photochemical A → B system was reported.¹⁶ A general method for analysing complex photochemical/thermal AB and ABC systems was reported in 2005, though this model assumes irradiation at an isosbestic point to render the photokinetic factor constant (*vide infra*).¹⁷ In more complex systems, where several photochemical and/or thermal conversions take place, closed expressions relating the reaction rates of all components have so far not been obtained. The majority of theoretical treatments have focused on a single process as part of an equilibrium.^{17,18} In the present system this is not the case: the primary concern is not the rate constant of a single process, but the overall rotation rate, which is a composite of all three reaction rates, and obtained *via* the number of thermal B → A conversions under a given set of conditions. As will be shown below, for high rotation rates the photokinetic factor $F(t)$ can be considered a constant at all irradiation wavelengths, not only in the case of irradiation at an isosbestic point, due to the fact that high rates of rotation are observed at low equilibrium conversions.

The photochemical-thermal equilibrium determining the overall rate of rotation of symmetric molecular motors is

Fig. 2 Equilibrium determining the rotation rate of molecular motors in solution.

presented in Fig. 2. Continuous rotation is achieved by performing irradiation at a temperature where k^Δ is non-zero. The maximum rotation rate ω° is given by an expression assuming a saturating flux of photons, which is similar to assuming maximum availability of B. Under these hypothetical conditions, the thermal helix inversion step is rate limiting; as each step represents one half rotation, the maximum rotation rate of a molecular motor is given by

$$\omega^\circ = \frac{1}{2}k^\Delta \quad (1)$$

However, this holds only when it is assumed that the concentration of B is not limited. However, in reality B is generated photochemically from A, and hence the rate equation for the equilibrium is given by:

$$\frac{\partial C_B(t)}{\partial t} = F(t)(\varepsilon_A \varphi_A C_A(t) - \varepsilon_B \varphi_B C_B(t)) - k^\Delta C_B(t) \quad (2)$$

In this expression, the rate of formation of B is governed by the molar absorptivities ε_X ($\text{l mol}^{-1} \text{cm}^{-1}$) of A and B, the quantum yield for the conversion of A to B, φ_A , the quantum yield for conversion of B to A, φ_B , the rate of thermal helix inversion k^Δ (s^{-1}) and the photokinetic factor $F(t)$. $F(t)$ in this analysis is directly related to the intensity of the light I_0 ($\text{mol cm}^{-2} \text{s}^{-1}$) and the total absorbance A of the system by:

$$F(t) = 1000 I_0 \left(\frac{1 - 10^{-A}}{A} \right) \quad (3)$$

In this expression, the total absorbance A of the system is given by:

$$A = l \times (\varepsilon_A C_A(t) + \varepsilon_B C_B(t)) \quad (4)$$

which means that the photochemical reaction rate is determined by the concentrations of A and B. However, because this system is a bimolecular equilibrium, it is governed at all times by the mass balance equation.

$$C_A(t) + C_B(t) = C_0 \quad (5)$$

When the total conversion to B is written as:

$$\alpha = \frac{C_B(t)}{C_A(t) + C_B(t)} \quad (6)$$

the following boundary conditions are obtained:

$$\begin{aligned} C_B(t) &= \alpha C_0 \\ C_A(t) &= (1 - \alpha)C_0 \end{aligned} \quad (7)$$

The rate equation (eqn (2)) can be rewritten in terms of the conversion α as:

$$\frac{\partial \alpha}{\partial t} = -(F(t)(\varepsilon_A \varphi_A + \varepsilon_B \varphi_B) + k^\Delta)\alpha + \varepsilon_A \varphi_A F(t) \quad (8)$$

At equilibrium $\partial \alpha / \partial t = 0$ which provides an expression for the conversion at equilibrium, where the concentrations of A and B remain constant under continuous irradiation. This equilibrium will be termed the rotational equilibrium, RE, under the present conditions.

$$\alpha^{\text{RE}} = \frac{\varepsilon_A \varphi_A F(t)}{F(t)(\varepsilon_A \varphi_A + \varepsilon_B \varphi_B) + k^\Delta} = \frac{\varepsilon_A \varphi_A}{\varepsilon_A \varphi_A + \varepsilon_B \varphi_B + \frac{k^\Delta}{F(t)}} \quad (9)$$

From eqn (9) the well-known expression for a photo-equilibrium is obtained by setting $k^\Delta \rightarrow 0$, which supports its validity. However, eqn (9) still displays dependence on the total absorbance A and the irradiation intensity I_0 by the expression for the photokinetic factor $F(t)$ (eqn (3)), which in turn is governed by the equilibrium position according to eqn (4).

Typical experimental conditions achieved in practice for determining the behaviour of molecular motors involved cooling the sample solution to a temperature where k^Δ is negligible. Irradiation for a set time period, depending on concentration and irradiation intensity, then results in establishment of a photochemical equilibrium involving A and B. However, if the temperature is sufficiently high, k^Δ becomes a significant factor in the equilibrium, so that significant net conversion is not observed. In this case, form B that is generated photochemically is converted to A as fast as it is formed. Generally, with rate constants k^Δ greater than $\sim 10^{-2} \text{s}^{-1}$ steady-state conversion to form B is too low for characterisation of the photochemical equilibrium. In this case, the spectral data of the irradiated solution under equilibrium conditions are equal to those obtained for A alone. Therefore, assuming that $k^\Delta > 10^{-1} \text{s}^{-1}$:

$$A(t) = l \times (\varepsilon_A C_A(t) + \varepsilon_B C_B(t)) = l \times \varepsilon_A \times C_0 \quad (10)$$

With this assumption, the photokinetic factor $F(t)$ loses its dependence on the concentrations of A and B, and hence on the equilibrium position. It is determined only by the total absorbance of the system, which is determined by the initial concentration C_0 and the irradiation intensity I_0 , which renders $F(t)$ effectively a constant. However, by using high photon fluxes, the conversion α may become significant. In such a case, the total absorbance of the system at the wavelength of irradiation may change depending on the magnitudes of ε_A and ε_B , and $F(t)$ will change accordingly. For this reason, the conversion α at equilibrium is dependent on the characteristics of the system. In this analysis, it is assumed that when $\alpha < 0.05$ eqn (10) holds.

The conversion at rotational equilibrium is determined solely by ε_A , the quantum yield for conversion of A to B, φ_A , the rate of the thermal reaction k^Δ and the photokinetic factor $F(t)$ at rotational equilibrium F^{RE} , which is itself determined by experimental parameters according to:

$$F^{\text{RE}} = 1000 I_0 \frac{1 - 10^{-\varepsilon_A C_0 l}}{\varepsilon_A C_0 l} \quad (11)$$

From this the overall rotation rate in solution ω is defined by the actual number of rotations per molecule per second, which is given by calculation of half the number of thermal $B \rightarrow A$ conversions per molecule (where the irradiation volume is smaller than the sample volume this expression has to be multiplied by the factor $V_{\text{irr}}/V_{\text{sample}}$):

$$\omega = \frac{\frac{1}{2}k^\Delta \alpha^{\text{RE}} C_0}{C_0} = \frac{1}{2}k^\Delta \alpha^{\text{RE}} \quad (12)$$

A factor Ψ can be defined based on the above equation, which describes the efficiency of rotation. It is given by the number of (directional) thermal $B \rightarrow A$ conversions over the total

number of $B \rightarrow A$ conversions; a value of $\Psi \rightarrow 1$ indicates perfect unidirectional behaviour (photochemical $B \rightarrow A$ conversion does not take place, *i.e.* the photochemical process is rate limiting) whereas $\Psi \rightarrow 0$ reflects a completely random photochemical equilibrium as $k^A \rightarrow 0$ (unidirectional motor behaviour is not observed, *i.e.* the thermal reaction is rate limiting).

$$\psi = \frac{k^A}{k^A + \varepsilon_B \varphi_B F(t)} \quad 0 \leq \psi \leq 1 \quad (13)$$

Rotation rate analysis

From eqn (1)–(13), the average number of rotations per molecule per second can be calculated on the basis of a fixed set of variables: four molecular parameters ε_A , ε_B , φ_A and φ_B , which are specific to the identity of the motor, and three external parameters I_0 , C_0 and k^A . I_0 can be varied by control of the light flux, C_0 determines the absorbance of the system, and k^A is related directly to temperature. A hypothetical system can be defined, with molecular parameters $\varepsilon_A = 5000 \text{ l mol}^{-1} \text{ cm}^{-1}$ and $\varepsilon_B = 2500 \text{ l mol}^{-1} \text{ cm}^{-1}$ at the irradiation wavelength and $\varphi_A = 0.1$ and $\varphi_B = 0.05$. The dependence of the rotation rate ω on the irradiation intensity I_0 and the total concentration of the system C_0 for different values of k^A is evaluated, retaining $\alpha < 0.05$ at all times.

The rate of rotation ω is dependent on the magnitude of the photokinetic factor, which is concentration-dependent (Fig. 3). At low concentration, $F(t)$ reaches a maximum value, which decays exponentially to 0 at higher concentration ($0 \leq (F(t)/1000I_0) \leq 2.3$). As can be seen from Fig. 3, at $10^{-5} \text{ l mol}^{-1} \text{ cm}^{-1}$ where $A = 0.1$ – 0.8 the photokinetic factor is below its maximum value; at higher concentrations an exponential decrease in photochemical reaction rates is observed due to the linear dependence of the rate on $F(t)$. This results in a strong decrease in the overall rotation rate. On the other hand, lower concentrations will not result in an increase in the photochemical reaction rate, despite the increase in the photon to molecule ratio.

Taking the rotation rate ω in a 10^{-5} M solution as an example, the following dependence on irradiation intensity I_0 for a series of rate constants k^A is obtained (Fig. 4–6).

Fig. 3 Dependence of the photokinetic factor $F(t)$ on the total absorbance of the system A for $I_0 = 10^{-10} \text{ mol cm}^{-2} \text{ s}^{-1}$.

The rotation rate ω increases linearly with irradiation intensity I_0 until a k^A -dependent ‘breakpoint’ is reached, from where the rotation rate cannot increase further by a further increase in I_0 . In the range where an increase in I_0 does not result in an increase in rotation rate the rotation can be termed ‘thermally rate limited’. As can be seen from Fig. 4, obtaining a thermally rate limited system requires intense irradiation, even at 10^{-5} – 10^{-6} M concentration. A thermal rate constant of 10^2 s^{-1} will be overall rate limiting only at irradiation intensities of $\sim 10^{-3} \text{ mol cm}^{-2} \text{ s}^{-1}$, which corresponds to 328 W at 365 nm over the full sample volume. Under these conditions the maximum rotation rate for this system (40 Hz) can be reached. This value does not correspond to the maximum rotation rate as defined by eqn (1) (50 Hz). This is due to the fact that in this hypothetical system, the values for ε_A , ε_B , φ_A and φ_B have been set as described above; when these values are replaced for 5000 , 1000 , 0.5 and 0.01 , respectively, the result is 49.9 Hz , approaching the theoretical maximum value for rotation in solution given a certain thermal rate constant.

Fig. 6 shows how the unidirectional quality of rotation Ψ is affected by the rate of the thermal step and the irradiation intensity at 10^{-5} M concentration. From this it is observed that a motor system, which is close to being thermally rate limited, undergoes a steep drop in Ψ from 1 to 0. This is interpreted as follows: where there is sufficient photon flux available to render the system thermally rate limited, the amount of photochemical $B \rightarrow A$ conversion will increase rapidly. In a system which is photochemically rate limited, thermal $B \rightarrow A$ conversion will occur much more frequently than photochemical $B \rightarrow A$ conversion, hence the unidirectionality factor approximates to 1 under such conditions.

In a similar analysis, the dependence of the overall rotation rate on concentration was investigated. The results can be seen in Fig. 7–9.

First, as mentioned in the discussion of $F(t)$, decreasing the concentration to increase the photon to molecule ratio only increases the overall rotation rate at relatively high concentrations. At typical experimental concentrations, depending modestly on the value of ε_A and ε_B , decreasing

Fig. 4 Dependence of the overall rotation rate ω on the irradiation intensity I_0 for several values of k^A .

Fig. 5 Dependence of the conversion at rotational equilibrium α on the irradiation intensity I_0 for several values of k^A .

Fig. 6 Dependence of the unidirectionality factor Ψ on the irradiation intensity I_0 for several values of k^A .

Fig. 7 Dependence of the overall rotation rate ω on the concentration C_0 for several values of k^A .

the concentration does not result in an increase in rotation speed at constant irradiation intensity. At concentrations

Fig. 8 Dependence of the conversion at rotational equilibrium α on the concentration C_0 for several values of k^A .

Fig. 9 Dependence of the unidirectionality factor Ψ on the concentration C_0 for several values of k^A .

lower than C_{break} the rotation rate stabilises, and the thermal process becomes the rate limiting process. However, a maximum overall rotation rate is reached, determined by I_0 , and increasing k^A or decreasing C_0 does not increase the overall rotation rate. In this regime, the system is 'photochemically rate limited'. The absolute values along the axes are especially notable: at 10^{-5} M at 328 W (10^{-3} mol cm $^{-2}$ s $^{-1}$) of 365 nm light, the maximum rotation rate achievable is close to 10 ^{3} Hz. Under these experimental conditions the conversion is below 0.05 as is required (Fig. 8). Furthermore, the unidirectionality factor Ψ is 1, and hence all photons absorbed that are used for *cis*–*trans* isomerisation result in photochemical A to B isomerisation, producing maximum efficiency.

In three dimensions, the dependences of overall rotation rate on k^A , I_0 and C_0 are represented in Fig. 10. Increasing irradiation intensity increases rotation speed until the system becomes thermally rate limited (plateau for $k^A = 10^3$ s $^{-1}$). However, photochemical rate limitation is more common, and is encountered in all cases where increasing k^A does not increase ω (overlap of fine and rough grids). When under such

Fig. 10 Correlation between rotation speed ω , irradiation intensity I_0 and concentration for a theoretical molecular motor with characteristics $\epsilon_A = 5000 \text{ l mol}^{-1} \text{ cm}^{-1}$, $\epsilon_B = 2500 \text{ l mol}^{-1} \text{ cm}^{-1}$, $\varphi_A = 0.01$ and $\varphi_B = 0.05$ for $k^\Delta = 10^7$ (rough grid) and $k^\Delta = 10^3$ (fine grid).

circumstances at high concentration the overall rotation rate can be increased further by decreasing the concentration, however this only holds until the plateau of photochemical rate limitation is reached. The maximum rotation speed of 3 MHz for the fastest molecular motor (k^Δ at 20 °C = $6.3 \times 10^6 \text{ s}^{-1}$)¹¹ under optimal conditions would require $3.3 \times 10^6 \text{ W}$ (365 nm) of continuous irradiation—a challenging experimental value.

Since empirical data regarding the average rotation rate under irradiation at a certain temperature are still unavailable, this theoretical approach presents the only means of analysis of what is reasonable to expect. When experimental techniques will become available that allow for determination of individual intramolecular transitions under static equilibrium conditions, these calculated results will require experimental confirmation. For the moment, however, given the possibility of developing molecular devices based on high-speed molecular motion, these results present an indication of what rates of motion may or may not be expected given a set of experimental parameters.

In general, when performing these calculations with a range of different motor characteristics, it is observed that the combined effect of quantum yields and molar absorptivities of A and B influence the rotation rate by at most half an order of magnitude when using reasonable values. This can be seen in Table 1, where a selection of values has been used to evaluate the final rotation speed for a thermally rate limited system. The rotation speed ω remains similar over a very wide range of absorptivities of A and B and quantum yields, and a 2500% increase in quantum yield does not increase the overall rotation rate (entries 3 and 4). The overall rotation rate ω is determined predominantly by the combination of I_0 , C_0 and k^Δ , and order of magnitude deviations of the maximum value can be achieved only by setting extremes in the motor parameters.

It should be noted however that under photochemical rate limiting conditions the effect of the photochemical characteristics of the system is more pronounced than with thermal rate limitation. In Table 2 a series of rotation rate determinations for the same hypothetical systems under such

Table 1 Rotation rates, equilibrium conversions and unidirectionality factors for a series of hypothetical molecular motors under thermal rate limitation ($I_0 = 10 \text{ mol cm}^{-2} \text{ s}^{-1}$, $k^\Delta = 10^4 \text{ s}^{-1}$, $C_0 = 10^{-6} \text{ M}$)

System	ϵ_A	φ_A	ϵ_B	φ_B	ω	α	Ψ
1	10^5	0.25	10^2	10^{-2}	5×10^3	1	2×10^{-4}
2	5000	0.25	2500	0.25	3.3×10^3	0.7	3×10^{-4}
3	2500	0.25	2500	0.25	2.5×10^3	0.5	7×10^{-4}
4	2500	0.01	2500	0.01	2.5×10^3	0.5	2×10^{-2}
5	2500	0.1	5000	0.25	8×10^2	0.2	2×10^{-3}

conditions is shown. Here it becomes apparent that the quantum yield and absorbance of A play a distinct role in determining the overall rotation rate, although the absorbance and quantum yield of B are of less influence.

In order to relate theory to the reality of experimental setups, calculations on two motor systems with known characteristics have been performed with the aim of determining an approximate rotation rate at room temperature. The motors have been characterised before,^{11,19} and are displayed in Fig. 11.

As no accurate determinations of photochemical quantum yields in the equilibrium governing rotation have been performed, in the current analysis $\varphi_A = \varphi_B = 0.5$ will be assumed for both cases, on the basis of comparison with stilbene photochemistry.^{13a,20} Furthermore, a sample solution of concentration $C_0 = 10^{-5} \text{ M}$ will be assumed, that is irradiated by CW laser irradiation at an intensity of 100 mW in a sample area of 0.5 mm^2 at the absorption maximum. This means the irradiation intensity is $6.5 \times 10^{-5} \text{ mol cm}^{-2} \text{ s}^{-1}$ for the case of **1**, and $6.3 \times 10^{-5} \text{ mol cm}^{-2} \text{ s}^{-1}$ for the case of **2**. The rate of rotation of **1** when irradiated at 386 nm is $\omega^\circ = 9.7 \times 10^{-4} \text{ Hz}$ under these conditions, and the system is thermally rate limited (Fig. 12, top). The conversion α^{RE} under these conditions is 0.54, so that the value of ω° should be considered an approximation, and the unidirectionality factor $\Psi = 3 \times 10^{-6}$. On the other hand, when subjecting **2** to the same experimental parameters, the system is photochemically rate limited, at a conversion $\alpha^{\text{RE}} = 5 \times 10^{-3}$. The average rotation rate ω° of **2** under these conditions is $6.9 \times 10^2 \text{ Hz}$ (Fig. 12, bottom), resulting in a unidirectionality factor $\Psi = 0.995$. This is the same order of magnitude at which ATPases are rotating, and approximately half of the rate of rotation of a flagella motor. However, although the change of motor represents a dramatic increase in the rate of rotation under the same experimental conditions, the analysis indicates that system **2** could theoretically be increased to an ω° of $1.1 \times 10^5 \text{ Hz}$, because it is far from being thermally rate limited; however, an irradiation intensity of $3 \times 10^4 \text{ W cm}^{-2}$ would be

Table 2 Rotation rates, equilibrium conversions and unidirectionality factors for a series of hypothetical molecular motors under photochemical rate limiting conditions ($I_0 = 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}$, $k^\Delta = 10^4 \text{ s}^{-1}$, $C_0 = 10^{-6} \text{ M}$)

	ϵ_A	φ_A	ϵ_B	φ_B	ω	α	Ψ
1	10^5	0.25	10^2	10^{-2}	2.9×10^{-2}	5.7×10^{-6}	1
2	5000	0.25	2500	0.25	1.4×10^{-2}	2.7×10^{-6}	1
3	2500	0.25	2500	0.25	7.2×10^{-3}	1.4×10^{-6}	1
4	2500	0.01	2500	0.01	2.9×10^{-4}	5.7×10^{-8}	1
5	2500	0.1	5000	0.25	2.9×10^{-3}	5.7×10^{-7}	1

Fig. 11 Motors **1** and **2** as benchmark cases for thermally- and photochemically-rate limited systems.

Fig. 12 Number of rotations ω° vs. irradiation intensity I_0 for **1** (top) and **2** (bottom).

required to reach more than 90% of the maximum possible number of rotations ($> 1 \times 10^5 \text{ Hz}$ at $1 \times 10^{-1} \text{ mol cm}^{-2} \text{ s}^{-1}$).

Conclusion

The development of molecular motors that display rate limiting thermal rates of $> 10^6 \text{ s}^{-1}$ requires an analysis of the overall average rotation rate in solution under the experimental conditions. A theoretical analysis shows that for a standard motor, the rotation rate is governed primarily by the irradiation intensity, the rate of the thermal reaction and the concentration, and that the influence of the quantum yields and absorptivities is much less pronounced. Nevertheless, intensities required to make a system reach thermal rate

limitation are much higher than previously anticipated, and as a result the effective rotation rate under realistic experimental conditions is less than theoretically possible. Two well-studied molecular motors serve as benchmarks for the case of thermal- and photochemical rate limitation, which indicates that though rotation rates of 10^2 Hz can be achieved under realistic experimental conditions, increasing the number of rotations to beyond MHz requires complex experimental design.

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