Plasmon-assisted click chemistry at low temperature: an inverse temperature effect on the reaction rate†

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Plasmon assistance promotes a range of chemical transformations by decreasing their activation energies. In a common case, thermal and plasmon assistance work synergistically: higher temperature results in higher plasmon-enhanced catalysis efficiency. Herein, we report an unexpected tenfold increase in the reaction efficiency of surface plasmon-assisted Huisgen dipolar azide–alkyne cycloaddition (AAC) when the reaction mixture is cooled from room temperature to −35 °C. We attribute the observed increase in the reaction efficiency to complete plasmon-induced annihilation of the reaction barrier, prolongation of plasmon lifetime, and decreased relaxation of plasmon-excited-states under cooling. Furthermore, control quenching experiments supported by theoretical calculations indicate that plasmon-mediated substrate excitation to an electronic triplet state may play the key role in plasmon-assisted chemical transformation. Last but not least, we demonstrated the possible applicability of plasmon assistance to biological systems by AAC coupling of biotin to gold nanoparticles performed at −35 °C.

Introduction

The illumination of metal nanostructures at wavelengths corresponding to the plasmon resonance maximum leads to collective excitation of free electron oscillations and generation of hot electrons.1–2 The excited electrons quickly reach non-equilibrium Fermi energy distribution through electron–electron scattering and then lose energy at a lower rate due to electron–phonon scattering.3–4 Within this time-window, a direct injection of electrons from the metal nanostructure or intramolecular electron excitation may occur in nearby organic molecules possessing suitable acceptor molecular orbitals.5–12 Excited organic molecules are then involved in (plasmon-assisted) chemical transformations.8–14

According to current theories, such plasmon-assisted reaction pathways include several events: (i) plasmon excitation of organic molecules by external electron injection or HOMO–LUMO intramolecular electron transition, (ii) vibrational relaxation of molecules in the excited state, and (iii) relaxation of an injected or excited electron, resulting in an “activated” molecule, which has a lower residual barrier for the desired chemical transformation.15 This residual barrier is then overcome by conventional heating.6 Under these assumptions, temperature and light act in synergy – the light excites plasmons, which activates the nearby molecule, while the temperature is responsible for overcoming the residual thermodynamic barrier.4,16,17 The relative importance of non-thermal and thermal effects in plasmon nanocatalysis is, however, far from being fully understood.18

The temperature dependence of plasmon-assisted reaction kinetics could differ significantly, depending on the value of the residual activation barrier and temperature impact on different stages of plasmon-assisted transformation(s).19–25 This may even result in the non-monotonic temperature dependence of the reaction rate as has been recently demonstrated for CO oxidation.26 In the special case of a completely vanished residual barrier, temperature effects on the lifetimes of excited electrons or molecular excited states can be expected to lead to inverse temperature dependence of the reaction rates: firstly, higher temperature could increase the electron–phonon scattering and thus decrease the plasmon lifetime and probability of the reactant excitation. Secondly, it could decrease the lifetime of...
the electronically excited molecules, making the desired reaction less probable. To the best of our knowledge, this phenomenon has not been demonstrated yet.

Despite the fact that organic plasmon nanocatalysis is a rapidly evolving field, detailed mechanisms of the initial stages of plasmon nanocatalysis remain elusive. We previously demonstrated that plasmon assistance can induce the azide–alkyne cycloaddition (AAC) reaction. AAC is an important biochemical coupling reaction performed either under heating or with the utilization of metal catalysts (Cu, Ru, etc.). Carrying out the AAC reaction at low temperatures could make it cleaner and accessible to more delicate substrates. In this study, we report unprecedented inverse temperature dependence observed for the plasmon-assisted AAC reaction and attempt to explain its origin by exploring the reaction mechanisms using the combination of theoretical and experimental approaches.

**Experimental procedures**

Used materials, preparation of initial reagents and grafted nanoparticles, measurement techniques and control experiments are described in the ESI.†

**Plasmon-driven azide–alkyne cycloaddition**

1 ml of suspension of AuNPs with attached 4-ethynylphenyl groups (further designated as AuNPs–C≡CH) in acetonitrile was mixed with 2 ml of 1 mM solution of 4-azidobenzoic acid, and the resulting mixture was illuminated for 3 hours with a light-emitting diode (LED) (660 nm emission wavelength, irradiance on the first reactor window ~ 20 mW mm\(^{-2}\)) in a controlled temperature chamber under magnetic stirring. The intensity of the LED irradiation was measured by using Photodiode Power Sensors (Thorlabs, S142C). After the reaction, the modified AuNPs were separated by centrifugation (7000 rpm, 20 min), washed with acetonitrile and methanol, and dispersed in methanol to a final volume of 0.5 ml. 0.1 ml of the resulting suspension was deposited on a silica substrate (0.5 cm × 0.5 cm) and dried at room temperature for further analysis.

**Results and discussion**

**Efficiency of plasmon-assisted azide–alkyne cycloaddition increases at lower temperature**

The reaction pathways were calculated with the Gaussian 16 rev. A03 program, employing density functional theory (DFT). Specifically, we used the B3LYP functional with D3 Grimme’s dispersion correction and the 6-311+G(d,p) basis set. All reported minima and transition state structures were confirmed by the calculation and diagonalization of their Hessian matrices. The reported energies are Gibbs free energies calculated with the SMD method in acetonitrile solvent at 298.15 K and the 1 bar standard state. The singlet excited state energies were calculated employing the TD-DFT method. The energy of \( S_0 \) was calculated with the non-equilibrium geometry and is therefore only a crude estimate.

The immobilization of 4-ethynylphenyl units was confirmed by Raman measurements (Fig. 1C and S1†). In the dry phase, we performed separate times for each temperature. In turn all SERS measurements were also repeated 5 times at different spots on the sample surface. The obtained SERS results were evaluated as averaged peak intensity with error bars corresponding to the deviation of characteristic signals from separated samples and uncertainty in the framework of single samples. Spectra were plotted according to ref. 33.
the +25 to −35 °C temperature range (melting point of acetonitrile is −45 °C, whereas viscosity at −35 °C is 0.9 mPa s and at +25 °C 0.4 mPa s). The SERS spectra recorded after the reaction performed at different temperatures are shown in Fig. 2A. The appearance of characteristic triazole ring SERS peaks and the simultaneous decrease of acetylene peak intensity are well evident at all temperatures. In turn, Fig. 2B and S3† show the evaluation of the characteristic SERS band ratio, corresponding to the consumption of acetylene groups and formation of triazole rings. The amounts of reacted acetylene groups as well as formed triazole rings slightly increase during the gradual reduction of the reaction temperature up to −10 °C. A further decrease in the reaction mixture temperature leads to a rapid increase of observed conversion, which becomes especially pronounced in the −20 °C to −30 °C temperature range. At temperatures near −30 °C the increase of the reaction rate reaches a plateau. Thus, we observed almost one order of magnitude increase of the reaction rate upon cooling the reaction from RT up to −35 °C. Control measurements indicate the absence of 4-ethynylphenyl group degradation as well as no formation of side-products (Fig. S5† and related discussion). In addition, the illumination of the reaction mixture, performed in the absence of plasmon-active nanoparticles, does not indicate any chemical conversion (see Fig. S6 and S7† and related discussion). Therefore, our results clearly show the increase of the AAC rate under the plasmon excitation and the fact that the decrease in temperature leads to a larger conversion of the alkyne reactant.

Mechanistic studies

We postulate that the plasmon assistance could significantly decrease the residual activation energy of AAC according the mechanism presented in Fig. 1B – i.e. via electronic excitation of reactant(s), their vibrational relaxation in an electronic excited state, and product formation through the residual activation barrier, overcoming of which often requires heating.44,45 However, heating can also increase the electron–phonon scattering and shorten the lifetime of plasmon-excited molecular states. Therefore, the heating of the reaction mixture can
negatively affect the reaction rate, if quantum effects prevail. So, the main question is which stage limits the reaction progress – probability of plasmon-assisted excitation of molecules, lifetime of excited molecules or overcoming the residual potential barrier?

To find the dominant rate-limiting effects in our case, we assessed the potential impact of viscosity increase, plasmon heating (which can be locally enhanced due to nanoparticle agglomeration with temperature decrease), damping of electron scattering, and prolongation of hot-electron lifetime at low temperatures (Fig. S8–S10† and related discussion), as well as performed DFT calculations of potential reaction pathways. First, experimental and theoretical estimations of nanoparticle agglomeration and related plasmonic local heating indicate the absence of apparent nanoparticle agglomeration and a moderate (approximately 1 K) increase of temperature in the close vicinity of metal nanoparticles under our experimental conditions (Fig. S9 and S10†). Indeed, the collective heating of the suspension of AuNPs, as well as a large temperature gradient near AuNP surface,46,47 does not allow us to completely exclude contributions from plasmon heating. At the same time, the inverse temperature dependence observed in our case is not consistent with plasmon heating as the main driving force of this plasmon-assisted chemical transformation.

Secondly, control experiments with the addition of PEG, performed at RT, do not result in comparable reaction acceleration, which could prove negligible viscosity influence on AAC progress (Fig. S11 and S12† and related discussion). Thirdly, the prolongation of the plasmon-excited electron lifetime was estimated from the temperature dependency of the Drude scattering parameter, taking into account the electron–phonon scattering in the bulk of AuNPs.48 Simple estimation of excited electron relaxation, performed on the basis of Holstein approximation, indicates the increase of their lifetime with temperature decrease by ~25%. Thus, the prolongation of the plasmonic excitation lifetime can explain only a fraction of the observed reaction speedup.

In DFT calculations, aimed at exploring potential AAC pathways, we focused on comparing the reactivity of differently activated phenylacetylene (Fig. 3A, reaction coordinates are given in the ESI†). Since the acetylene moieties were spatially separated from AuNPs (Fig. 1), we did not consider their interactions with the gold surface. Two common modes of plasmonic activation were considered: injection of hot electrons from metal nanoparticles or intramolecular HOMO–LUMO electron excitation. As a baseline, we show the thermal pathway of the AAC reaction (designated as PW0) in Fig. 3A. This reaction type represents Huisgen pericyclic [3 + 2] dipolar cycloaddition, where the product is formed via a single cyclic transition state TS0 through an energy barrier of 124 kJ mol⁻¹ in a concerted manner.

Next, we considered the plasmon-assisted electron excitation of the alkyne to a triplet T1 state (PW1), which corresponds to energy-transfer catalysis. The energy needed to form the T1 state is larger than the energy of a single 660 nm photon (181 kJ mol⁻¹). Indeed, the dependence of the reaction rate on the laser power was found to be nonlinear (Fig. S13†), which indicates the contribution from multiphoton absorption processes. This contribution becomes even more pronounced at ~35 °C. Product formation from the T1 state would start by C–N bond formation via TS1, accompanied by the spin density transfer to the azide unit. Int1 formed in this process can

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Fig. 2  (A) SERS spectra, recorded on AuNP arrays after a plasmon-induced click reaction on the nanoparticle surface performed at different temperatures; (B) dependence of reaction conversion (estimated as the increase of I₂₂₃⁵/I₁₅₉₀ and the decrease of I₂₀₀₀/I₁₅₉₀ SERS peak ratios) on the temperature.
undergo ring closure via $\text{TS}_{T2}$ to give a triplet state of the product, which finally undergoes intersystem crossing (ISC) to $P$. The ISC might also take place in earlier steps in the reaction path, for example after the formation of $\text{TS}_{T1}$, because they are all higher in energy than the TS in the ground state and would thus have sufficient energy to overcome the barrier leading to $P$. If the triplet excitation is transferred to the azide molecule via the Dexter mechanism without the concomitant C–N bond formation, it would lead to instant elimination of the nitrogen molecule and formation of triplet nitrene ($\text{TS}_{T1}$nitrogen), which would react with the acetonitrile solvent and would not stay bound to the nanoparticles. If the $\text{PW1}$ reaction coordinate is indeed operational, it could contribute to the observed reaction rate temperature dependence, since decreasing temperature, besides the prolongation of the plasmon lifetime, slows down the relaxation of the triplet state $T_1$, and therefore increases the probability that it encounters a suitably positioned azide reactant.

In the case of plasmon assistance through hot electron injection (photoredox catalysis), we considered two possibilities. The first one ($\text{PW2}$ in Fig. 3A) involves the reaction of the thus formed phenylacetylene radical-anion with azide in a stepwise manner. We found different transition states for the formation of the first bond differing in the orientation of reactants in the $\text{TSR1}$– and $\text{TSR3}$– transition states. Subsequently, we were able to find the remaining intermediate $\text{IntR}$ and transition state $\text{TSR2}$– leading to the observed product from $\text{TSR1}$–. However, the almost isoenergetic $\text{TSR3}$– leads to the expulsion of the nitrogen molecule, which indicated that the reaction pathway $\text{PW2}$ should lead to the formation of sizeable amounts of by-products.

The second possible reaction pathway ($\text{PW3}$ in Fig. 3A) considers the activation of the phenylacetylene molecule by first forming the phenylacetylene radical-anion and subsequent loss of the injected electron and reaction of vibrationally excited...
phenylacetylene $S_{0}$ with azide. In this case, a vibrational energy of 59 kJ mol$^{-1}$ could lower the reaction barrier of the concerted process, but since it is much less than 124 kJ mol$^{-1}$ required to reach $T_{S}$, and this path cannot be responsible for the observed temperature dependence. We also briefly considered the activation of the phenylacetylene substrate with hot holes, analogous to the recently proposed photoredox AAC mechanism (PW4 in Fig. 3A), and this pathway also did not lead to a substantial decrease of the reaction barrier and is thus not likely operative.

To get further insight, and see whether PW1 or PW2 are in operation, we performed control experiments with the addition of TEMPO, a scavenger of radicals that should block both PW2 and PW3, and addition of cyclooctatetraene (COT), a scavenger of the triplet excited state, that should block PW1 (Fig. 3B and C). As can be seen in Fig. 3C, the addition of both compounds decreases the conversion at lower temperature. The effect of COT, however, was found to be significantly higher (Fig. 3 and S14†). Even the addition of a negligible amount of COT (10$^{-6}$ M) results in almost complete suppression of triazole formation at RT and at $-35 \degree C$. Additional control experiments involving cyclohexene and 4-cyanobenzoic acid (see Fig. S15 and S16† and related discussion) indicate that the impact of COT should be attributed mostly to excited state quenching. However, we also observed moderate inhibition of the reaction with 4-cyanobenzoic acid, which may be attributed to the partial blocking of surface reaction sites. Overall, the results of plasmon-assisted experiments performed with scavengers of radicals or excited states do not exclude the hot-electron injection related reaction pathway but indicate that PW1 should be viewed as the dominant mechanism. In addition, the different effects of the individual additives also run counter to the dominant effect of viscosity or the local heating effect.

We also checked the ability of the “reverse” AAC initiation, through the grafting of azide chemical moieties onto the AuNP surface in reaction with phenylacetylene dissolved in acetonitrile under plasmon excitation at $-35 \degree C$ (Fig. S16†). In this case, we did not detect the appearance of a reaction product. The singlet-triplet gap in the azide is much smaller than in the alkyn (ca. 150 kJ mol$^{-1}$) and thus triplet azide does not have enough energy to overcome the energy barrier of $T_{S}$.

Finally, we compared our results with the catalytic efficiency of common Cu catalysts (Fig. 2B, C, and S7F†). It can be seen that plasmon assistance has similar efficiency to the Cu catalyst at RT and significantly greater efficiency at $-35 \degree C$. Moreover, control experiments with COT addition and Cu-based catalyst do not indicate any changes in the reaction rate. Therefore, the measured effect of reaction quenching by COT points to the involvement of the plasmon-excited molecular triplet state (or triplet state transfer).

Taken together, we find that the PW1 mechanism is the most plausible, because it couples the release of a large amount of thermal energy (up to 280 kJ mol$^{-1}$) from the triplet state of the alkyn with the physical proximity of the other reacting partner (azide). As a result, there is effectively no residual barrier, which is fully consistent with the observed reverse temperature behaviour of the reaction rate.

**AAC coupling of biotin**

High reaction temperatures or utilization of toxic catalysis leads to lower reaction selectivity, restricts the reaction scope, and thus restricts the applicability for biorganic transformations. To demonstrate the advantages of plasmon-assisted AAC at low temperature, we performed the coupling of biotin azide to AuNPs–C≡CH. Biotin is widely used for the detection of cellular alkyn cholesterol, preparation of a novel multifunctional benzophenone linker for pull-down assays, and photoaffinity labelling of double-click stapling techniques. Classically, the AAC of biotin is performed with copper-based catalysts, which can sometimes be undesirable due to the presence of traces of copper in reaction products.

The schematic representation of biotin coupling with 4-ethynylphenyl moieties on AuNPs is presented in Fig. 4 (top) and the results of plasmon-assisted AAC performed at $-35 \degree C$ without the addition of catalysts are shown in Fig. 4 (bottom). The SERS spectrum of biotin-azide is also presented for comparison (peak assignment is given in Table S2†). The comparison of the Raman spectra of biotin-azide powder and AuNPs coupled with biotin by plasmon-induced AAC shows that the reaction proceeds with a high yield (estimated as the decrease of the C≡C vibration band) at sub-zero temperature under copper-free conditions. This shows that our protocol is applicable to the AAC reactions of more complex substrates without the addition of metal catalysts or heating.

**Fig. 4**  SERS spectrum of biotin-azide and SERS spectra recorded on AuNPs–C≡CH before and after conjugation with biotin-azide, performed at $-35 \degree C$ with plasmon assistance.
Conclusions

Plasmon assistance promotes a range of chemical transformations through lowering of the activation energy and the synergy between the heating of the reaction mixture and plasmon assistance is well described in the field of plasmonic chemistry. Here, we theoretically and experimentally demonstrated the opposite situation, where the decrease of reaction temperature led to a significant increase of plasmon-assisted catalytic efficiency. To model and explain the details of the complex process, we utilized an AAC reaction on the surface of spherical gold nanoparticles. The maximum reaction rate is observed at temperatures significantly below zero and it significantly exceeds the efficiency of common Cu-based catalysis. Density functional theory calculations identify several barrierless AAC pathways under plasmon assistance. Control experiments with cyclooctatetraene (triplet quencher) point to significantly below zero and it

Author contributions

O. G. performed the experiments; J. V. performed the quantum calculations; L. T. P. performed the experiments; I. P. designed the experiments; L. R. designed the calculations; A. T. performed the numerical calculations; P. P. analyzed the results; V. S. designed the experiments; E. A. analyzed the theoretical results and wrote the manuscript; O. L. analyzed the experimental results and wrote the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the Grant Agency of the Czech Republic (project 18-26170S), the Czech Ministry of Education, Youth and Sports (LTAUSA19148), the Tomsk Polytechnic University Competitiveness Enhancement Program.

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