

Kinetics of Oxidation of Azide by [Ethylenebis(biguanide)]silver(III) in Aqueous Acidic Media

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In aqueous acidic media sodium azide and the orange-yellow title complex react quantitatively generating N₂ gas along with a colourless solution of Ag⁺ ion and the ligand, ethylenebis(biguanide). The parent complex, [Ag(H₂L)]³⁺, and one of its conjugate bases, [Ag(HL)]²⁺, participate in the reaction with N₃[−] as the kinetically reactive reductant. Ag⁺ has no catalytic effect. At 25.0 °C, *I* = 1.0 M (NaNO₃), rate con-

stants for the reactions [Ag(H₂L)]³⁺ + N₃[−] and that for [Ag(HL)]²⁺ + N₃[−] are (12.3±0.5) and (3.8±0.6) M^{−1}·s^{−1}, respectively. The high rate constants along with the very low equilibrium constant (10^{−15} M^{−1}) calculated for the first reaction strongly suggest inner-sphere redox mechanism. (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2003)

Introduction

Ethylenebis(biguanide)silver(III) (Figure 1) represents the simplest cationic complex^[1–3] of Ag^{III} stable in aqueous solution over a wide pH range against dechelation and intramolecular redox decomposition.^[4] The square-planar acyclic tetraaza ligand imparts fascinating thermodynamic stability^[5] to the Ag^{III} state and renders the title complex a milder oxidant^[6] than Ag⁺. It is a potential inner-sphere oxidant,^[7–11] which may bind a reducing ligand in its vacant axial coordination sites. But in this strong-field d⁸ system such ligand binding is likely to be weak or at best moderate. Hence, outer-sphere reactions may be energetically more favourable^[12,13] for weakly basic but strongly reducing ligands with the Ag^{III} complex. In redox reactions the complex may act as either a one-^[7] or a two-electron^[10] oxidant. In solution the title complex undergoes ligand-based protic

equilibria.^[14] Also, the Ag^{III}-bound ligand, H₂L may form hydrogen bonds with a suitable reducing agent, like HC₂O₄[−] and lead to a dead-end adduct in the electron-transfer pathway.^[15] The mechanistic versatility of oxidations of various organic and inorganic species by the title Ag^{III} complex is an outcome of such properties as discussed above.

Kirschenbaum et al. studied^[16] the oxidation of N₃[−] by Ag(OH)₄[−] in strongly alkaline media. They found that the N₃[−] ion replaced a coordinated hydroxide ion in Ag(OH)₄[−] and the azido complex so produced underwent subsequent redox decay with another N₃[−] ion. Sengupta et al. proposed an analogous mechanism^[17] for the oxidation of N₃[−] by [Ag(H₂TeO₆)₂]^{5−}, again in strongly alkaline media. We are not aware of any mechanistic study of azide oxidation by higher valent silver species in acidic media. The exceptional stability of the title complex towards redox decomposition in acidic media affords a good chance to examine for the first time the reactivity of HN₃ and N₃[−] towards a cationic Ag^{III} complex in acidic solutions. Moreover, the ligand H₂L in [Ag(H₂L)]³⁺ is substitution-inert so that Ag^{III} never comes free in solution to open up extra, complicating pathways in its kinetics.

Results and Discussion

Preliminary Observations

In the absence of any external buffer, the media pH before and after the reactions did not change by more than 0.05 units. Autodecomposition of the Ag^{III} complex was insignificant under the experimental conditions of pH and temperature. No Ag⁺ catalysis (studied up to 0.01 M) was found in the reactions. We did not extend the reaction pH

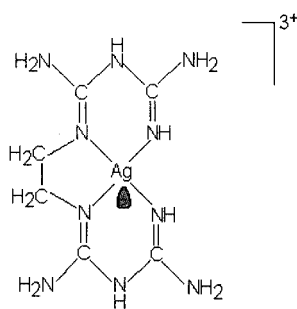


Figure 1. Structure of [Ag(H₂L)]³⁺; the gray-shaded area represents a weakly bonded ClO₄[−] ion at the axial site

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> ca. 4.05, as reaction mixtures above pH $\approx$ 4.2 turn turbid probably due to formation of insoluble silver azide after ca. 30% decrease in their initial absorbances, thus seriously interfering with the kinetic measurements.

Stoichiometry and Reaction Products

Stoichiometric measurements yielded $\Delta[\text{Ag}^{\text{III}}]_{\text{T}}/\Delta T_{\text{R}} = 0.52 \pm 0.05$. The principal conversion can thus be represented by Equation (1).



The oxidation of azide to dinitrogen was qualitatively confirmed by GC analysis. Immediately after completion of the reaction (absorbance < 0.01 at 380 nm), the solution pH was raised to ca. 5 by adding NaOH solutions when all Ag^+ was precipitated as AgN_3 and removed by filtration. From the filtrate, the free ligand ethylenebis(biguanide) was quantitatively isolated^[18] as the sparingly soluble [ethylenebis(biguanide)]copper(II) sulfate, and the amount of Cu^{II} thus held was estimated iodometrically after decomposing the Cu^{II} complex. The results showed that more than 95% of the free ligand (H_2L) was recovered.

Kinetics

No immediate spectral changes were observed on mixing the reactants over the entire experimental range of pH. But the absorbance of the reaction mixtures at $\lambda \geq 380$ nm gradually decreased to less than 0.01 and the $\log_{10}(\text{absorbance})/\text{time}$ plots were found to be linear to 90% completion of the reactions. The first-order rate constants, k_{obs} , defined by Equation (2) were obtained from least-squares slopes of these plots.

$$-d[\text{Ag}^{\text{III}}]/dt = k_{\text{obs}}[\text{Ag}^{\text{III}}] \quad (2)$$

Averages of the k_{obs} values (Table 1) from at least three independent runs were taken and the average coefficients of variation (CV) for these measurements were within 3%.

The reaction was found to be first-order in T_{R} ($= [\text{HN}_3] + [\text{N}_3^-]$) and there is no T_{R} -independent term. The following changes of the reaction conditions had, within the limits of experimental uncertainties, no influence on the values of k_{obs} : a fivefold variation in $[\text{Ag}^{\text{III}}]$ from 0.10 to 0.50 mM, addition of AgNO_3 up to 0.01 M, addition of ethylenebis(biguanide) up to 1.0 mM, occasional shaking of the spectrophotometer cell, presence or absence of dissolved oxygen and diffused light, and a variation in the monitoring wavelength in the range 380–480 nm.

No polymer formed when 6% (v/v) acrylonitrile was added to the reaction mixture and the entire reaction course was EPR-silent. These experiments therefore indicate that free radicals or other paramagnetic species like Ag^{II} do not accumulate in the reaction media in concentrations detectable by either of these two methods.

The value of k_{obs} sharply decreases with increasing $[\text{H}^+]$. A plot of k_{obs} versus $[\text{H}^+]^{-1}$ at a fixed T_{R} (Figure 2) is a

Table 1. Some representative first-order rate constants for the oxidation of azide by the Ag^{III} complex

pH	T_{R} [mM]	$10^4 k_0$ [s^{-1}] ^[a]	CV in % ^[b]
1.00	3.0	0.24 (0.24)	3.0
1.50		0.76 (0.76)	3.0
2.00		2.35 (2.34)	2.5
2.65		10.0 (9.9)	2.6
2.90		16.8 (16.7)	2.1
3.35		39.2 (38.4)	2.3
3.70		60.0 (62.8)	2.3
4.05		84.0 ^[c] (86.8)	3.0
1.01	30.0	2.29 (2.44)	2.8
1.50	6.0	1.56 (1.51)	3.0
1.50	12.0	3.10 (3.02)	2.9
2.00	12.0	9.20 (9.36)	2.2
2.02	6.0	5.00 (4.93)	2.6
2.05	24.0	22.0 (21.1)	2.6
2.05	30.0	25.8 (26.4)	2.7
2.50	15.0	34.2 (36.0)	2.0
2.52	30.0	70.0 (74.9)	2.1
2.90	1.5	8.30 (8.35)	3.0
2.90	6.0	33.0 (33.4)	2.1
2.90	12.0	65.5 (66.8)	1.8
3.05	6.0	44.5 (44.9)	1.9
3.05	12.0	88.0 (89.8)	1.9
3.10	1.5	12.1 (12.4)	2.0
3.10	3.0	24.2 (24.8)	2.0
3.35	3.0	37.3 (38.4)	2.8
3.35	6.0	76.0 (76.8)	1.9
3.55	1.5	25.4 (26.0)	2.9
3.55	6.0	107 (104)	1.8
3.85	1.5	36.2 (37.0)	2.2
3.85	6.0	143 (148)	1.9
4.05	1.5	42.5 (43.4)	2.8

^[a] [complex] = 0.20 mM, $T = 25.0$ °C, $I = 1.0$ M (NaNO_3). Calculated k_{obs} values are given in parentheses. ^[b] CV was measured using the relation: $\text{CV} = \text{sd} \times 100/x$, where sd = standard deviation of the measurements of k_{obs} and x = average k_{obs} . See ref.^[19], p. 1123. ^[c] $10^4 k_{\text{obs}}$ [s^{-1}] values are 91.0, 97.0 and 106 at $I = 0.5$, 0.2 and 0.1 M respectively.

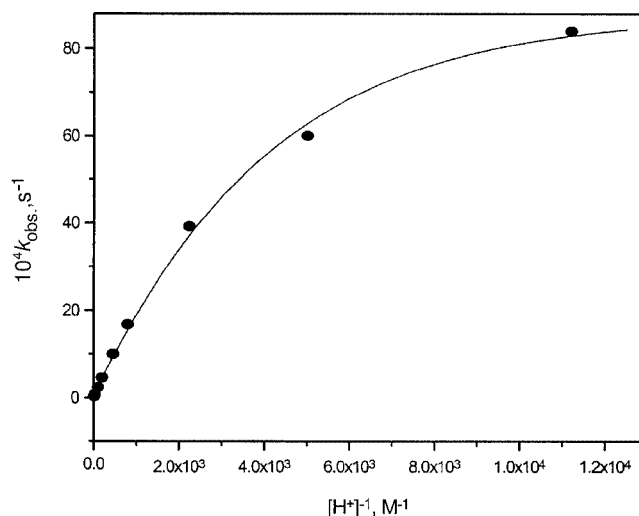
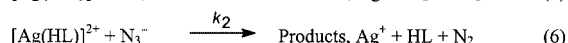
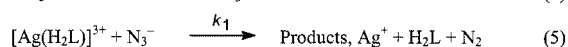
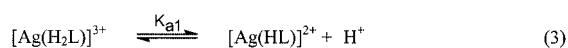


Figure 2. Plot of k_{obs} versus $[\text{H}^+]^{-1}$ at $T_{\text{R}} = 3.0$ mM; the solid line represents the fit of Equation (7)

good straight line for $\text{pH} \leq 2.9$ ($[\text{H}^+] \geq 1.26 \cdot 10^{-3} \text{ M}$) with zero intercept but droops at higher $[\text{H}^+]^{-1}$. Such $[\text{H}^+]$ dependence of k_{obs} indicates that the conjugate base form of one of the reactants is more reactive while that of the other is less reactive than the parent acid. We infer that N_3^- is much more reactive than HN_3 while $[\text{Ag}(\text{H}_2\text{L})]^{3+}$ is more reactive than its conjugate base, $[\text{Ag}(\text{HL})]^{2+}$. This is expected from known kinetic behaviour^[11,12,19,20] of these species and the fact^[21,22] that protonation generally increases the reactivity of metal complex oxidants whereas the anionic forms of protolytic reductants are much more reactive than the uncharged molecular compounds.^[23–25] The near-zero value for k_{obs} at high $[\text{H}^+]$ further suggests that kinetic activity of HN_3 is negligible for the present system. The scheme in Equations (3) to (6) most simply accommodates the kinetic observations and the known acid/base equilibria K_{a1} and K_{a} .



The derived rate-law for this scheme is Equation (7).

$$k_{\text{obs}}(K_{\text{a1}} + [\text{H}^+])(K_{\text{a}} + [\text{H}^+])/T_{\text{R}} = k_1 K_{\text{a1}}[\text{H}^+] + k_2 K_{\text{a1}} K_{\text{a}} \quad (7)$$

A plot of the left hand side of Equation (7) versus $[\text{H}^+]$ is a good straight line (Figure 3, $r = 0.99$) with slope = $(8.0 \pm 0.3) \times 10^{-4} \text{ s}^{-1}$ and intercept = $(3.9 \pm 0.6) \times 10^{-8} \text{ M} \cdot \text{s}^{-1}$. Using known K_{a} ($= 6.5 \cdot 10^{-5} \text{ M}$)^[26] and K_{a1} ($= 1.585 \cdot 10^{-4} \text{ M}$)^[14] values, these lead to $k_1 = (12.3 \pm 0.5) \text{ M}^{-1} \cdot \text{s}^{-1}$ and $k_2 = (3.8 \pm 0.6) \text{ M}^{-1} \cdot \text{s}^{-1}$. These rate constants reproduced all experimental k_{obs} values satisfactorily (Table 1).

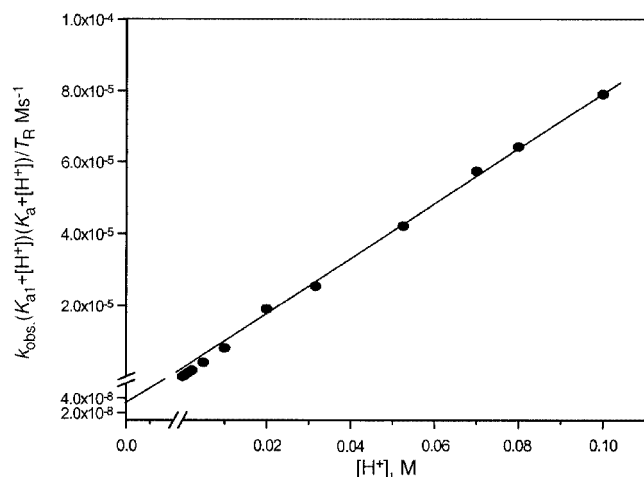
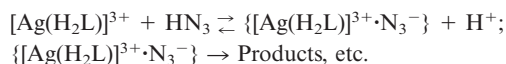


Figure 3. Plot of $k_{\text{obs}}(K_{\text{a1}} + [\text{H}^+])(K_{\text{a}} + [\text{H}^+])/T_{\text{R}}$ versus $[\text{H}^+]$; the solid line represents the fit of Equation (7)

Mechanism

The redox potentials for the couple $[\text{Ag}(\text{H}_2\text{L})]^{3+/2+}$ and that for N_3^-/N_3 are 0.43 V^[27,6] and 1.33 V^[28] respectively. The self-exchange rate constant^[28] for N_3^-/N_3 is $4 \cdot 10^4 \text{ M}^{-1} \cdot \text{s}^{-1}$ and the upper limit for the self-exchange rate for $[\text{Ag}(\text{H}_2\text{L})]^{3+/2+}$ has been estimated^[27] to be $10^{6.6}$. With these values and using the Marcus cross-relation,^[29] $k_{12} = (k_{11}k_{22}K)^{1/2}$, the calculated maximum value of the outer-sphere oxidation rate of N_3^- by $[\text{Ag}(\text{H}_2\text{L})]^{3+}$ is $10^{-4} \text{ M}^{-1} \cdot \text{s}^{-1}$, considerable less (10^5 times) than k_1 and we therefore propose an inner-sphere mechanism for the k_1 path. An inner-sphere mechanism appears very likely for the k_2 path, too. Indeed, the very high thermodynamic price for the oxidation of N_3^- to N_3 essentially requires strong oxidants^[30,31] like $[\text{Ni}(\text{bipy})_3]^{3+}$ or $[\text{CoW}_{12}\text{O}_{40}]^{5-}$ for outer-sphere reactions to occur.

Coordination of the azide ion to the metal centers^[16,17,32–34] in $[\text{Ag}^{\text{III}}(\text{OH})_4]^-$, $[\text{Ag}^{\text{III}}(\text{H}_2\text{TeO}_6)_2]^{5-}$, $[\text{Cu}^{\text{III}}(\text{H}_2\text{TeO}_6)_2]^{5-}$, $[\text{Mn}^{\text{III}}(\text{bipy})_2(\text{OH})]^{2+}$, $[\text{Mn}^{\text{III}}(\text{edta})(\text{H}_2\text{O})]^-$, or in $\text{Mn}_{\text{aq}}^{3+}$ are well documented with the formation constants of azido complexes lying in the range 10^{-1} to 10^2 . A similar azide binding is likely for the Ag^{III} complex under investigation. X-ray photoelectron spectroscopic measurements^[35] have shown that the silver(III) centre in the title complex has a high degree of positive charge resulting in a high electron affinity of the Ag^{III} ion. Expectedly, therefore, structural^[36–38] and kinetic studies^[8,9,11] indicated axial coordination by Ag^{III} with low molecular weight alcohols, H_2O_2 , SO_4^{2-} , NO_3^- , or even ClO_4^- . The kinetic steps (5) and (6) are therefore most likely to proceed via intermediate adduct formations between Ag^{III} and N_3^- followed by intramolecular redox decomposition to form the final products. The present results cannot straightaway eliminate the possibility of proton-ambiguous paths like

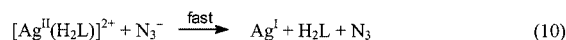
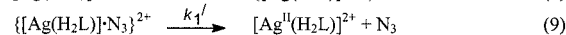
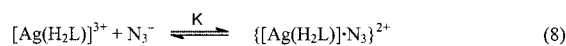


Nevertheless, the observed increase in reaction rate with decreased ionic strength of the reaction media does not fit into this alternative reaction scheme, rather it directs the reaction between oppositely charged ions. Also, it has been established that N_3^- is kinetically far more reactive than HN_3 and may exhibit overwhelming kinetic dominance over HN_3 ^[30,39] even for redox reactions in 1 M acid.

In the lower pH range ($\text{pH} \leq 2.9$), where $[\text{Ag}(\text{H}_2\text{L})]^{3+}$ is the only active and sole oxidant, the rate law simplifies to $k_{\text{obs}}/T_{\text{R}} = kK_{\text{a}}/[\text{H}^+]$. The observed linearity of the k_{obs} versus $[\text{H}^+]^{-1}$ plot at higher $[\text{H}^+]$ demands a maximum value of the order of 10^1 M^{-1} for preequilibrium formation of any adduct between $[\text{Ag}(\text{H}_2\text{L})]^{3+}$ and N_3^- . $[\text{Ag}(\text{HL})]^{2+}$, a possible weaker Lewis acid than its conjugate acid should bind N_3^- even less tightly.

The present kinetic observations cannot unambiguously settle the question of one- or two-electron transfer. The immediate one-electron oxidation product^[28,40–44] of azide is N_3 , as firmly established by pulse radiolysis, flash photolysis or by molecular beam studies. The azidyl radical (N_3)

may decay to N_2 in several ways, like by fragmentation^[45] to N_2 and N , the process, although spin-forbidden, is close to thermoneutral^[46] with a rate constant^[47,48] around 10^6 s^{-1} . In yet another possibility, N_3 can combine with N_3^- forming^[49–51] N_6^- (however, attempts to observe the radical dimer N_6^- using pulse radiolysis met with no success,^[48b] but nanosecond laser flash photolysis^[50,51] and kinetic evidences^[16] suggest involvement of N_6^- in some instances) and then rapid reaction of N_6^- with the oxidant species or a rapid direct reaction of two mol of N_3 radical could produce three mol of N_2 ($2 N_3 \rightarrow 3 N_2$, $2k = 9 \cdot 10^9 \text{ M}^{-1} \cdot \text{s}^{-1}$).^[28] The absence of EPR evidence for Ag^{II} or N_3 radicals in our study cannot conclusively eliminate the formation of such species as it may only indicate that such species are formed but decayed too rapidly before they can diffuse into the bulk solvent sufficiently quickly to permit detection. For example, Equations (8) to (12) are one conceivable expansion for the k_1 path.



Reaction (9) requires a very high thermodynamic price and is as such unfavourable. Yet, the very high protonation constants^[52] of the ligand H_2L drag the overall reaction to completion in acidic media.

An alternative for the assigned fate of the azidyl radical could be the dimerisation to produce N_6 that ultimately produces N_2 . But, this appears unlikely here as, if it were the actual pathway, then sufficient accumulation of N_3 to cause appreciable reversal of reaction (9) and hence rate retardation (deviation from simple first-order kinetics) could be anticipated.^[48b,53] No such retardation could be detected and thus the dimerisation pathway is neglected in the present study.

Though the silver(III) complex under investigation is far more stable than $[Ag(OH)_4]^-$ or $[Ag(TeO_4)_2(OH)_4]^{5-}$, it oxidises N_3^- at a faster rate. This can be attributed to a difference in mechanism operating in these oxidations, for example, two-electron transfer in $[Ag(OH)_3N_3]^-$ or in $[Ag(TeO_4)_2(OH)_3(N_3)]^{5-}$ and the proposed one-electron transfer in our inner-sphere adducts. A reactive species ambiguity (HN_3 versus N_3^-) may also be a reason for obtaining a higher rate in the present investigation. However, of these two alternatives, the first appears more logical but the proton-ambiguity situation is unresolvable. The tetraaza ligand is expected to stabilise Ag^{II} much more than that by hydroxide or tellurate.

Direct two-electron changes in these redox steps to form N_3^+ which reacts with N_3^- forming N_6 and ultimately decays to N_2 cannot be ruled out in principle. Formation of N_3^+ has been proposed for the thermal decomposition^[54] of $[Mn(N_3)_2]^{2+}$ and photoinduced reductive decomposition

of $cis-[Pt(N_3)_2(PPh_3)_2]$ has provided distinct spectral evidence for the intermediate formation^[55] of neutral cyclic hexazine, N_6 .

Experimental Section

Materials: The silver(III) complex, $[Ag(H_2L)]^{3+}$, was prepared by a known procedure.^[3,56] Sodium azide (G. R., E. Merck) solutions were standardised by Ce^{IV} titration.^[57] $NaNO_3$ (G. R., E. Merck) solutions were standardised by passing an aliquot through a Dowex 50W X-8 strong cation exchange resin in the H^+ form and titrating the liberated acid with standard $NaOH$ to a phenolphthalein endpoint. To avoid any possible interaction of azide with oxides of nitrogen,^[58] the stock HNO_3 solutions were purged with argon before use. All measurements were made at 25.0°C and $I = 1.0 \text{ M}$ ($NaNO_3$). All solutions were prepared in water which was deionised and then doubly distilled.

Physical Measurements and Kinetics: UV/Vis spectra were recorded with a Shimadzu (1601 PC) spectrophotometer using 1.00-cm quartz cells. Kinetics were generally monitored at 380 nm in situ in the thermostatted ($25.0 \pm 0.1^\circ \text{C}$) cell-housing (CPS, 240A). For faster reactions sodium azide solutions (adjusted to the desired pH) were directly injected into the spectrophotometer cell containing other components of the reaction mixture at the same pH. The desired concentrations of the complex and the reducing agent were achieved after mixing which was immediately followed by automatic monitoring of the change in absorbance with time. We used capped quartz cells with minimum vacant space left and thus avoided escape of volatile HN_3 . The solution pH (1.00–4.05) was measured with a Systronics (India) pH meter (model 335) with electrodes calibrated as described earlier.^[59] All such pH measurements were done quickly to ensure minimum evaporation of volatile HN_3 . Spectrophotometric determination^[60] of azide in blank experiments indicated a near quantitative ($\geq 97\%$) recovery of total azide under our experimental conditions. Excess reducing agent, $T_R (= [HN_3] + [N_3^-])$, 1.5–30.0 mM over the complex (0.20 mM) was used in all kinetic runs.

Stoichiometry and Reaction Products: The reaction stoichiometry was determined under kinetic conditions in the pH range 3.5–4.0 by estimating unchanged azide spectrophotometrically. Excess azide was mixed with the complex solutions and stored until the reaction mixtures turned colourless indicating complete reduction of Ag^{III} to Ag^I . $Fe(NO_3)_3$ solution in 0.5 M HNO_3 was then added to the product mixtures^[60] to achieve $[Fe^{III}]/T_R$ in the final solutions within the range 1.5–2.5. The pH of the solutions was then adjusted^[60] to 1.5–2.0 using HNO_3 or $NaOH$, as needed. A red complex, $[Fe(H_2O)_5N_3]^{2+}$, generated within minutes. Its absorbance at 460 nm yielded the concentration of unchanged azide from a calibration curve constructed under comparable conditions ($\epsilon = 3570 \text{ M}^{-1} \cdot \text{cm}^{-1}$, literature value,^[60] $3680 \text{ M}^{-1} \cdot \text{cm}^{-1}$). We verified that Ag^+ or the ligand, ethylenebis(biguanide), do not interfere with the measurement of the azide concentration. The gaseous product formed during the reactions was collected over a saturated sodium chloride solution as described earlier^[61] and analysed by gas chromatography using a Chemito (India) GCHT 8610 equipped with TCD, a Porapak Q and molecular sieves 13 X column. Splitless mode injection of 500 μL of sample was used. The oven temperature, injector and detector temperature were kept at 40, 55, and 100°C , respectively. The carrier hydrogen gas flow was adjusted to 30 mL/min.

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