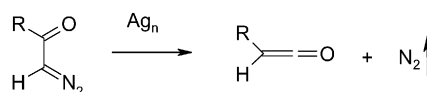


Evidence for the Involvement of Silver Nanoclusters during the Wolff Rearrangement of α -Diazoketones[†]Surendra G. Sudrik,^{*,‡} Trupti Maddanimath,[§] Nirmalya K. Chaki,[§] Sambhaji P. Chavan,[‡] Subhash P. Chavan,[‡] Harikisan R. Sonawane,[‡] and K. Vijayamohan^{*,§}Division of Organic Chemistry: Technology and Physical and Materials Chemistry
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Received May 5, 2003

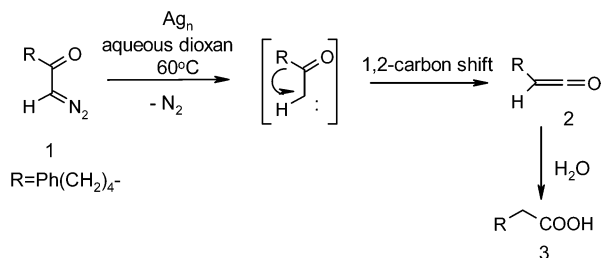
ABSTRACT



In situ-generated silver nanoclusters (Ag_n) during the reduction of either silver(I) oxide or other salts presumably catalyze the Wolff rearrangement of α -diazoketones. Their optical, physical, and catalytic properties depend on the starting silver(I) compound and the reaction conditions.

The (*Z*)-configuration-specific Wolff rearrangement^{1–5} of α -diazocarbonyl compounds is an integral part of the well-known Arndt–Eistert one-carbon homologation of carboxylic acids. In addition, it serves as a powerful technique for achieving the ring contraction of cyclic α -diazoketones (Scheme-1). The rearrangement involves a stereospecific 1,2-

Scheme 1



carbon shift following or accompanying the loss of dinitrogen to ketene via a transient, singlet α -ketocarbene^{6–8} intermedi-

ate. The α -elimination of dinitrogen can be initiated under the influence of thermal energy, ultraviolet light, transition metal catalysts, ultrasound⁹ in the presence of silver(I) ions, or more recently by microwave.^{10,11} Among these, transition metal catalysis is widely practiced, as the literature is replete with the use of several silver(I) catalysts, although the use of rhodium(II) complexes or copper(II) oxide is sparse. Silver(I) nitrate along with aqueous ammonia,⁵ silver(I) oxide in the presence of either triethylamine^{12,13} (Et_3N) or sodium

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[†] Dedicated to Prof. M. S. Wadia, Department of Chemistry, University of Pune, Pune-411 007, India, on the occasion of his 65th birthday.

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Table 1. Features of Silver Nanoclusters (Ag_n) Formed under Various Conditions of Silver(I) Catalysis of the α -Diazoketone^a

	silver(I) compd		silver nanoclusters (Ag_n)		
			UV-vis λ_{max} (nm)	particle size (nm)	yield of 3 (%)
i	AgOCOPh	Et ₃ N	308	0.5–15	91
ii	AgNO ₃	NH ₃	304	1–10	86 ^b
iii	Ag ₂ O	Et ₃ N	433	250 ^c	87
iv	Ag ₂ O	Na ₂ S ₂ O ₃	436	258 ^d	92
v	Ag ₂ O		347	1–5	68
vi	AgOCOPh		308, 440	1–14	76

^a General Procedure. The silver catalyst (5 wt % α -diazoketone) and either silver nanoclusters (Ag_n) prepared following the appropriate literature procedure^{5,12–14,16} excluding the α -diazoketone at room temperature (for cases i–iv) or the silver(I) compound (for the cases v and vi) is added in small portions at the regular interval of 20 min to the aqueous 1,4-dioxane solution of 2-hexanone-1-diazo-6-phenyl **1** (0.1 M) at 60 °C until the complete decomposition of **1** (0.5 h to 1 h). A usual solvent extractive workup followed by purification furnished the Wolff rearrangement product **3**, which matched the reported physical and spectral characteristics. ^b Chromatographically isolated yield of an amide of the carboxylic acid **3**. ^c TEM core size. ^d From SEM images.

thiosulfate,¹⁴ and silver(I) benzoate^{15,16} (AgOCOPh) in combination with Et₃N are more frequently used. The use of coreagents along with silver(I) compounds leads to a more reproducible¹⁵ formation of the rearrangement product in relatively higher yields at much lower temperatures. For example, AgOCOPh^{15,16} in combination with Et₃N catalyzes the Wolff rearrangement of α -diazoketones at room temperature. Although several suggestions such as reduction of the activation energy, solvent action on the silver(I) compounds leading to catalysis under homogeneous conditions or as a base to abstract the most acidic α -hydrogen resulting in the formation of carbanion have been made, the exact role of these additives is not well understood.

In this communication, we reveal for the first time experimental proof^{17–19} that electron donation by the additives to silver(I) compounds leads to the formation of silver nanoclusters (Ag_n) during the reaction, which presumably catalyzes the Wolff rearrangement of α -diazoketones. The latter feature is further confirmed by the formation of 6-phenyl-hexanoic acid **3** from α -diazoketone **1** following the portion wise addition of preformed silver nanoclusters²⁰ (Table 1; entries i–iv). The evidence from the surface plasmon absorption¹⁸ of the silver nanocluster formed during the reaction along with transmission electron micrographs

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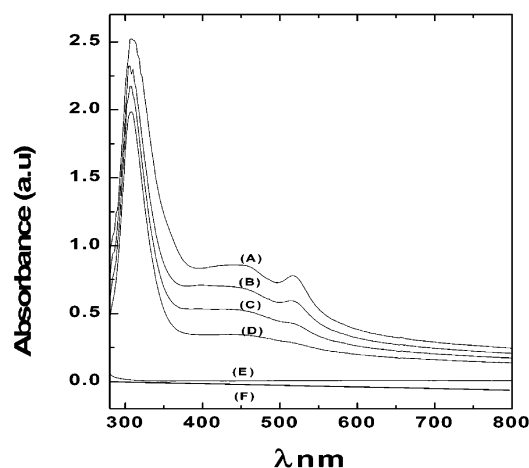


Figure 1. UV-visible spectroscopic followup of the formation of Newman's silver reagent prepared by mixing triethylamine and silver(I) benzoate for (A) 1 min, (B) 5 min, (C) 10 min, (D) 15 min; UV-visible spectra in aqueous 1,4-dioxane of (E) triethylamine, (F) silver(I) benzoate.

(TEM) give unambiguous confirmation for the involvement of nanoclusters. These results may prove to be germane to the understanding of the catalysis of several organic reactions by metal nanoclusters, especially the correlation of cluster size with catalytic activity.

Transitory formation of an orange color during the preparation of Newman's silver reagent^{15,16} using AgOCOPh and Et₃N kindled our curiosity to know more about the nature of silver catalyst. UV-visible spectroscopy (Figure 1) reveals the presence of a charge-transfer absorption band between $\lambda = 517$ and 308 nm. With increasing time, the absorption in the visible region diminishes in intensity along with a concomitant rise in the peak intensity in the ultraviolet region. Significantly, this latter absorption (around $\lambda = 308$ nm) corresponds to the surface plasmon characteristic of silver nanoclusters (Ag_n).¹⁸ It is relevant to note that silver ions are devoid of any UV-visible absorption, while metallic silver absorbs in the vacuum ultraviolet region. The plasmon absorption peak at $\lambda = 308$ nm (Figure 1) shifts bathochromically with time to give a relatively stable optical response around $\lambda = 436$ nm after about 12 h (Figure 2A and Supporting Information). This phenomenon can be understood in terms of the growth of particles of chemically identical silver clusters (Ag_n). TEM and selected area electron diffraction (SAED) at various regions of the sample specimen taken at different intervals provide conclusive evidence in this direction. For example, the TEM image obtained after half an hour (Figure-3A) show the presence of nearly monodispersed spherical particles having an average size of 1.4 nm ($\sigma \pm 0.048$), while similar analysis performed after 12 h (Figure 3B) exhibits the formation of relatively larger clusters (0.5–15 nm) with an average particle size of 4.6 nm ($\sigma \pm 4.2$). Importantly, all the electron diffraction patterns (inset of Figure 3) are identical to the structure of metallic silver (FCC, $a = 4.104$ Å). In addition, the silver surface

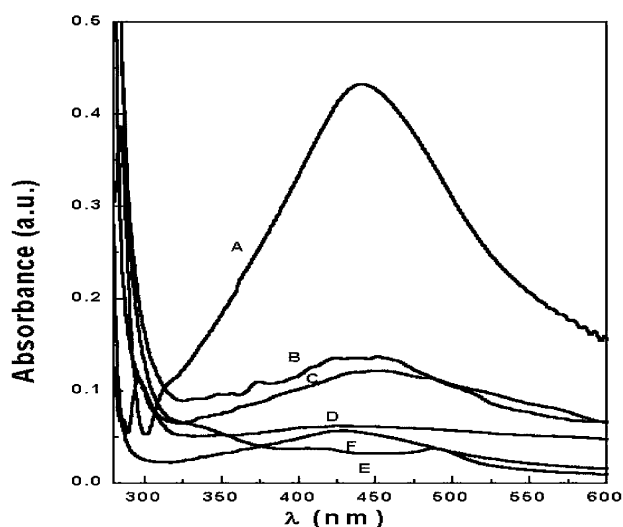


Figure 2. UV–visible spectra of Newman’s silver reagent (Ag_n) in various solvents: (A) toluene, (B) dichloromethane, (C) 1,4-dioxan, (D) methanol, (E) acetonitrile, and (F) *N,N*-dimethylformamide.

plasmon is strongly influenced by the dielectric constant of the medium (Figure-2), another significant feature of these Ag_n clusters. More specifically, with increasing dielectric constant, the strong absorption at $\lambda = 439$ nm in toluene with full width at half-maxima (fwhm) of 55.39 nm is gradually suppressed to show a nearly plateau-like nature

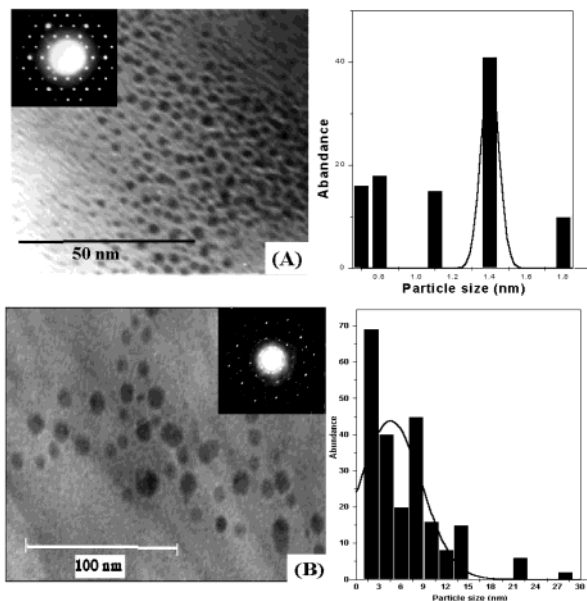
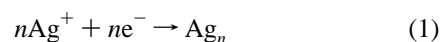


Figure 3. Transmission electron micrographs of Newman’s silver reagent prepared using silver(I) benzoate and triethylamine at different time intervals of (A) 0.5 h and (B) 12 h along with particle size distribution. The corresponding electron diffraction pattern is shown in the inset.

around $\lambda = 436$ nm in *N,N*-dimethyl formamide (dielectric constant = 37, fwhm = 110 nm), which indicates the charged nature and the self-organization ability of Ag_n clusters in the medium. These clusters are dispersed in organic solvents such as toluene and methanol. This intrinsic physical property¹⁷ of the metal nanoclusters arises due to their unique structure, in which the hydrophilic part of the capping agent (carboxylic acid, primary and secondary amine or thiols) is attached to the metal atoms, while the hydrophobic part protrudes into the solvent. These structural features are prominently reflected in the infrared (IR) and proton magnetic resonance (PMR) analysis (Supporting Information). Due to the attachment of a carboxylic acid group to silver atoms, the IR spectrum shows a strong band centered around 3440 cm^{-1} corresponding to a $\text{Ag}_n\text{--O}$ stretching along with a bathochromically shifted carbonyl band around 1660 cm^{-1} as compared to the sharp carbonyl absorption at 1716 cm^{-1} for benzoic acid. In addition, the spectrum shows a characteristic C=C stretching absorption around 1601 cm^{-1} . The PMR spectrum further confirms the presence of benzoic acid as the capping agent. Significantly, the fine splitting pattern of five contiguous aromatic protons, observed in the case of benzoic acid and AgOCOPh , collapses to give two broad resonances around $\delta = 7.42$ and 8.03 , respectively, indicative of the paramagnetic nature of this Ag_n . Ag_n catalysis of the α -diazoketone **1** in aqueous dioxane furnishes the 6-phenylhexanoic acid **3** in 91% yield (Table 1). The TEM image obtained after completion of the reaction shows the presence of relatively larger and polydispersed nanoclusters ranging from 10 to 80 nm. This phenomenon of cluster formation can be attributed to the unique ability of Et_3N to function simultaneously as an electron donor²¹ and cluster-stabilizing agent¹⁷ during the transition from atom to cluster.



The UV–visible followup (Figure 4A) and subsequent TEM analysis (Table 1) reveals the nature of the well-known ammoniacal silver reagent⁵ prepared using silver(I) nitrate and aqueous ammonia as polydispersed Ag_n ranging from 1 to 10 nm in diameter, presumably stabilized by ammonia. Aqueous sodium thiosulfate¹⁴ can function as an electron donor²² leading to the reduction of silver(I) oxide (eq 2).²² Interestingly, the resulting bare silver clusters self-assemble on the silver oxide surface, giving rise to a porous three-dimensional secondary network with diffused boundaries composed of uniformly sized (250 nm) grains as judged from scanning electron micrographs (SEM, Figure 5). The composition analysis by energy-dispersive X-ray analysis (EDAX) confirms the sole presence of silver on the surface in contrast to the presence of silver and oxygen atoms in the silver(I) oxide. These drastic changes in surface composition and morphology are responsible for the reproducible and enhanced catalytic activity. These structural changes were

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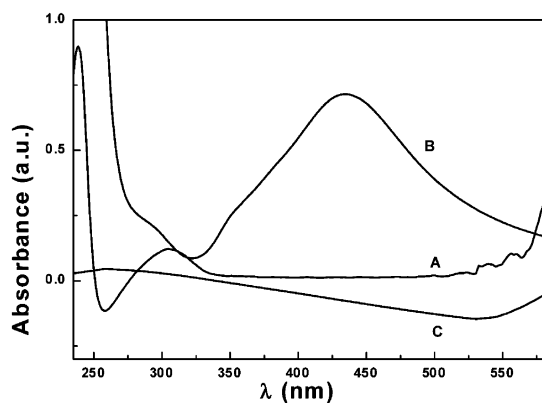


Figure 4. UV-visible absorption spectra recorded after 2 min of silver nanocluster formation under various conditions in (A) aq 1,4-dioxan, (B) AgNO_3 and aq NH_3 , and (C) AgOCOPh and 2-hexanone-1-diazo-6-phenyl.

further confirmed by the powder X-ray diffraction (XRD, Supporting Information) pattern, which shows the presence of both Ag_n [(111), (311), (220), (200)] and silver(I) oxide [(111) (100) (110) (113)]. Similar results were obtained using triethylamine (TEA) with silver(I) oxide (Figure 4B and

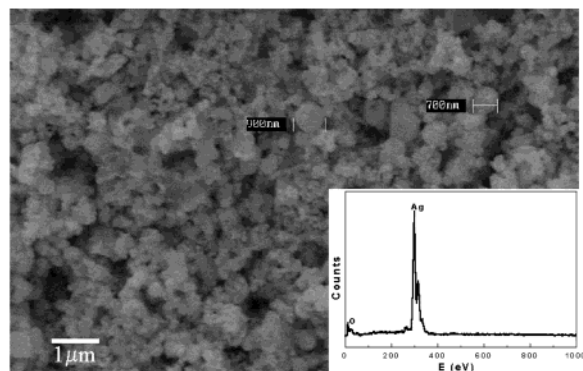
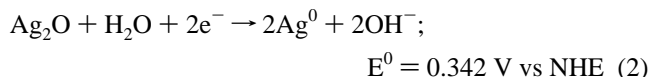


Figure 5. Scanning electron micrographs of the silver agglomerate formed during the reaction between sodium thiosulfate and silver(I) oxide in aq dioxane; the inset shows the elemental analysis using energy-dispersive X-ray analysis.

Table 1). These particles of silver also efficiently catalyze the Wolff rearrangement of the α -diazoketone **1** (Table 1).

Reactions of α -diazocarbonyl compounds catalyzed by either silver(I) oxide or AgOCOPh alone has a relatively large induction period until the copious evolution of nitrogen begins. UV-visible and TEM images recorded during the course of the reaction between silver(I) oxide and α -diazoketone **1** show that the reaction proceeds rapidly after the formation of polydispersed Ag_n ranging from 1 to 5 nm in diameter, due to the removal of an electron from α -diazoketone by silver(I) oxide.²³ Similarly, AgOCOPh accepts an electron from the α -diazoketone **1** to yield polydispersed benzoic acid-capped Ag_n (Figure 4C), as encountered earlier (vide supra). Ensuing results are summarized in Table 1.



In conclusion, we have shown that silver(I) compounds accept an electron either from various coreagents or α -diazoketone to form silver atoms that spontaneously grow into silver nanoclusters. Their optical, physical, and catalytic properties vary strongly as a function of size, which in turn is governed by the starting silver(I) compound and the reaction conditions. Chemists have unknowingly used these morsels of silver as a representative of the rapidly growing area of nanotechnology²⁴ to efficiently catalyze the Wolff rearrangement of α -diazoketones. Work to understand the mechanism of the catalytic process and size-dependent chemistry is in progress.

Acknowledgment. S.G.S. thanks Council of Scientific and Industrial Research (CSIR), New Delhi, for the award of a Research Associateship, while T.M., N.K.C., and S.P.C. thank CSIR for awards of Senior Research Fellowships.

Supporting Information Available: Time-dependent UV-visible spectra, IR, ^1H NMR, and XRD of silver nanocluster. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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