

Efficient conversion of NO into N₂O by selected electroreduced heteropolyanions

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It is shown that a series of one- and two-electron-reduced heteropolyanions of the Keggin- and Dawson-types convert quantitatively NO into N₂O in acidic aqueous media. The corresponding oxidized forms of the heteropolyanions are fully regenerated. Unsubstituted and lacunary heteropolyanions, as well as the substituted heteropolyanions of these two groups, prove active in this context.

Transformaion quantitative de NO en N₂O par des hétéropolyanions électroréduits. De nombreux hétéropolyanions ayant la structure de Keggin ou celle de Dawson présentent un comportement catalytique vis à vis de la réduction de NO, au potentiel de leur première vague de réduction. Les composés saturés ou lacunaires, et les substitués appartenant à ces deux groupes de structures, se révèlent efficaces pour cette réduction. Sur quelques exemples d'hétéropolyanions, dont le premier couple rédox est soit monoélectronique, soit biélectronique, il a été montré que la transformation de NO en N₂O est quantitative.

Among the large variety of catalytic processes in which heteropolyanions intervene efficiently in the liquid phase, our group has been interested in the reduction of nitrogen oxides for several years. Patents issued from this laboratory describe electrocatalytic procedures based on oxometalates for the reduction of nitrite anion and nitric oxide.^{1,2} Based on unambiguous cyclic voltammetric experiments, it was demonstrated that a large variety of Keggin-type as well as Dawson-type anions were suitable for this purpose. These families were extended by their lacunary transition-metal-substituted derivatives.^{1,2} Almost concomitantly, Toth and Anson³ published work that also demonstrated that Keggin-type iron-substituted polyoxometalates catalyze the reduction of nitrite and nitric oxide; this occurs primarily through the formation of an iron-nitrosyl complex that is further reduced at more negative potentials by electrons accumulated in the tungsten framework. The product obtained was ammonia. These two pioneering works aroused the interest of other groups.^{4–6} Most data from these groups corroborated the cyclic voltammetry work of Toth and Anson on iron-substituted heteropolyanions with an extension to Dawson-type anions^{4,6} and to some other transition metal cations.⁶ Confirmation of the data concerning the catalytic behaviour of the lacunary and the parent unsubstituted heteropolyanions in our patents also began to appear.^{4,6} None of them go beyond the results in the patents. Thus, a series of problems remains to be solved. They include, in particular, the identification and quantification of the products obtained on the catalytic waves and the mechanistic pathways through which the catalysis proceeds. These are currently under investigation in our group. Recently, we have published an attempt at an extension to suitable experimental conditions to obtain sizeable amounts of chemicals.⁷ The main product, detected after electrolysis at potentials more negative than the first redox couple of the heteropolyanions in this work, was N₂O.⁷

The aim of the present communication is to try and detect, and then to quantify, the products of the catalytic process. Owing to the high capacity of heteropolyanions to accumulate electrons in their framework and then deliver them to an

appropriate substrate, and also to the several reduction possibilities of nitrogen oxides, it seemed desirable to tackle the problem by steps. In the following, we are interested in the product (or products) obtained by the interaction of NO with the first electronation step of any heteropolyanion. Nitric oxide has been selected as the substrate to avoid the possible disproportionation process associated with nitrite anion at pH ≤ 3.

The mounting and polishing of the glassy carbon electrode (GC, Tokai, Japon, and V25 Le Carbone Lorraine, France) and the electrochemical set-up have been described previously.⁷ Analyses were performed on a Girdel 3000 gas chromatograph and on a Perkin Elmer Lambda 5 spectrophotometer. The gas chromatograph was equipped with a Porapack Q column for the analysis of N₂O and a 5 Å molecular sieve column for N₂. NH₂OH and N₂H₄ have been analyzed by cyclic voltammetry with a platinum electrode. The gases are injected directly into the chromatograph using a gas-tight syringe. Hyponitrous acid was analysed by UV-visible spectroscopy at 207 nm after precipitation of P₂W₁₈O₆₂^{6–} by NEt₄⁺.

Na₂SO₄, H₂SO₄ and HClO₄ (Prolabo) were used as received. The heteropolyanions (HPAs) were synthesized, purified and characterized by one of us, and the syntheses of those requiring new methods have been published.^{8,9} All the compounds are listed below and their abbreviations will designate the corresponding anions or the compounds themselves when no confusion seems possible: Na₆P₂Mo₁₈O₆₂ (P₂Mo₁₈), K₆P₂W₁₈O₆₂ (P₂W₁₈), α₁ and α₂FeP₂W₁₇O₆₁ (α₁ and α₂FeP₂W₁₇), α₂K₇FeP₂W₁₅Mo₂O₆₁ (α₂FeP₂W₁₅Mo₂), K₁₀P₂W₁₅Mo₂O₆₁ (P₂W₁₅Mo₂), α₁ and α₂K₆P₂W₁₇MoO₆₂ (α₁ and α₂P₂W₁₇Mo), K₆P₂W₁₅Mo₃O₆₂ (P₂W₁₅Mo₃), K₆P₂W₁₄Mo₄O₆₂ (P₂W₁₄Mo₄), K₆P₂W₁₂Mo₆O₆₂ (P₂W₁₂Mo₆), α₁K₉LiP₂W₁₇O₆₁ (α₁P₂W₁₇), α₂K₁₀P₂W₁₇O₆₁ (α₂P₂W₁₇), H₄SiMo₁₂O₄₀ (SiMo₁₂), (NH₄)₄SiW₁₂O₄₀ (SiW₁₂).

The reduction of NO by one- or two-electron-reduced HPAs has been carried out under an argon atmosphere in 0.2 M Na₂SO₄/H₂SO₄ (the pH 1 medium) by mixing two

solutions: one saturated with NO and the other containing the reduced HPA, usually called heteropolyblue (HPB). The solution of HPB was obtained under an argon atmosphere, in a two-compartment cell, by exhaustive electrolytic reduction and coulometry (one- or two-electron reduction) by setting the working electrode (glassy carbon sheet of 5 cm² surface area) potential at 60 mV negative to the peak potential observed in cyclic voltammetry for the first reduction process of the HPA. The HPB solutions are stored under argon in a flask tightly stoppered by a septum. Pure NO (N20 grade, Air Liquide France) was purified by bubbling through a 4 M NaOH solution (to get rid of N₂O and NO₂ impurities), then washed by bubbling through fully deionized Millipore water. The whole set-up was deaerated for at least one hour before introducing NO for purification. This purified gas was bubbled for at least 15 min into 50 ml of the thoroughly argon-deaerated pH 1 solution. The NO-saturated solution was also protected against dioxygen by tight septum stoppers. The NO was assayed by UV-visible spectroscopy in the presence of Fe^{II}(EDTA) as the complexing agent. The absorbance reading at 430 nm indicates a concentration of 1.5×10^{-3} M NO at room temperature. The NO-saturated solution was withdrawn by a gas-tight syringe and injected directly into the HPB solution. Completion of the reaction was indicated by the disappearance of the HPB colour. Then, 2 to 3 ml of concentrated HClO₄ were added to the mixture to facilitate gas evolution. Warming of the mixture to roughly 70 °C allows all the gas to be collected.

The efficiency of several HPAs for the catalysis of NO was first evaluated qualitatively in cyclic voltammetry experiments. P₂Mo₁₈ is chosen as a representative example. Its cyclic voltammogram in aqueous media begins by at least two two-electron reversible redox processes;^{10,11} only the first one is of interest in the present study. Fig. 1 was recorded with a thoroughly polished glassy carbon electrode in the pH 1 medium and shows the following main observations in sequence. The first three redox waves of P₂Mo₁₈ are well-behaved in the absence of NO (dotted line, Fig. 1A). Upon saturation of the HPA solution with NO, the current intensities of these waves are remarkably enhanced (full line, Fig. 1A) and their polarogram shapes can be used to evaluate the reaction rate constant. However, further interpretation of the morphology of these catalytic waves and the study of the associated mechanistic pathways and rate constants are beyond the scope of this paper and will be published elsewhere. In this short communication, only the phenomena concerning the first wave of the HPAs retain our interest and are better sketched in Fig. 1B. In the absence of HPA, nitric oxide is reduced close to the supporting electrolyte discharge. The improvement in operational potential ΔE_i for the reduction of NO brought about by the presence of the reduced HPA has been evaluated. For this purpose, a current density of 53 $\mu\text{A cm}^{-2}$ for the reduction of NO alone is chosen. ΔE_i is defined as the difference between the potential values at which this current density is observed in the absence and in the presence of catalyst, provided the catalyst current is subtracted. The overall rate constant evaluated from the polarogram-shaped catalytic wave¹² in Fig. 1B is $4.6 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$; roughly the same value, $5 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$, was obtained by double potential step chronocoulometry.¹³ Table 1 gives ΔE_i for a series of unsubstituted, lacunary and substituted HPAs, as well as the results for the catalytic efficiency defined as $\text{CAT} = 100 [I_p(\text{HPA} + \text{NO}) - I_p(\text{HPA})]/I_p(\text{HPA})$.

All the HPAs in Table 1, and the others cited in this communication, show the same kind of catalytic effects on their respective first redox couples in the presence of NO. The choice of HPAs has been made to highlight the very large ΔE_i values that could be achieved in the present experiments. Many details are worth noting. We observe from the current intensities of the catalytic waves that even the very favourable

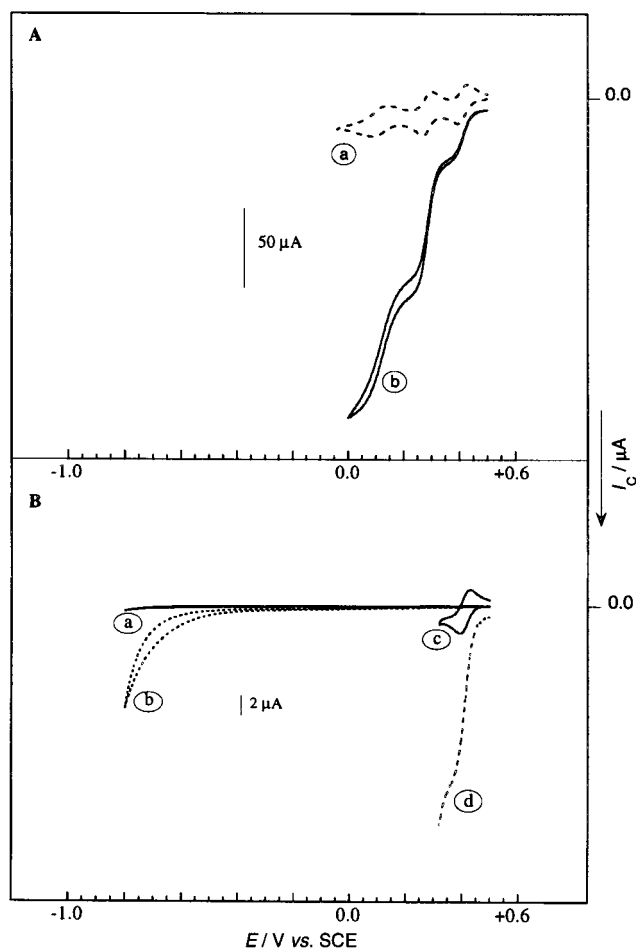


Fig. 1 Cyclic voltammograms in a pH 1 medium at a scan rate of 10 mV s⁻¹. Working electrode: 5 mm diameter glassy carbon disk; solutions deaerated with pure argon. (A) Dotted line: cyclic voltammogram in supporting electrolyte with 10⁻⁴ M P₂Mo₁₈O₆₂⁶⁻, showing the first three redox systems of the HPA under an argon atmosphere (the current intensity has been multiplied by 5). Full line: cyclic voltammogram of the preceding solution saturated with NO (the current intensity has been multiplied by 2). The parameter $\gamma = [\text{NO}]/[\text{HPA}] = 15$. (B) (a) Supporting electrolyte alone; (b) supporting electrolyte saturated with NO; (c) supporting electrolyte with 10⁻⁴ M P₂Mo₁₈O₆₂⁶⁻, thoroughly deaerated with argon; and (d) solution c saturated with NO

Table 1 Improvement in the operational potential ΔE_i obtained for the reduction of NO in the presence of heteropolyanions in pH 1 medium^a

HPA ^b	$\Delta E_i/\text{V}^c$	CAT (%) ^c
P ₂ Mo ₁₈	1.200	475
P ₂ W ₁₂ Mo ₆	1.200	344
α_1 P ₂ W ₁₇ Mo	1.080	900
SiMo ₁₂	1.070	1160
P ₂ W ₁₈	0.810	1150

^a The ΔE_i values are determined for a current density of 53 mA cm⁻² after subtraction of the HPA current. This current density, in the absence of heteropolyanion, is obtained at -0.8 V vs. SCE for NO-saturated solutions. Working electrode surface area: 0.19 cm². $\gamma = [\text{NO}]/[\text{HPA}] = 15$. ^b Only the five HPAs for which the yields for the NO reduction product were studied are listed. Numerous other HPAs, namely, P₂W₁₄Mo₄, P₂W₁₅Mo₃, α_2 P₂W₁₇Mo, α_2 FeP₂W₁₅Mo₂, P₂W₁₅Mo₂, α_1 and α_2 FeP₂W₁₇, α_1 and α_2 P₂W₁₇, and SiW₁₂, have been used under appropriate conditions and give very good results, which will be published elsewhere. ^c Scan rate of 10 mV s⁻¹.

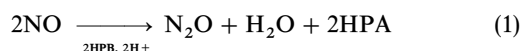
Table 2 Reduction of NO into N₂O by selected one- and two-electron-reduced HPAs^a

HPA	C°/mM	Electrolysis potential vs. SCE/V	Moles of HPA reduced (× 10 ⁶)	Moles of N ₂ O produced (× 10 ⁶)	Y (%) ^b
One-electron-reducible HPAs					
α ₁ P ₂ W ₁₇ Mo	1.7	+0.1	8.5	4.4	103 ± 6
	3.5	+0.1	17.5	8.8	100 ± 6
P ₂ W ₁₈	1 ^c	−0.06	5	2.4	96 ± 6
	2	−0.06	10	5.2	104 ± 6
	6	−0.06	30	15	100 ± 6
Two-electron-reducible HPAs					
P ₂ Mo ₁₈	1	+0.32	5.2	5.2	100 ± 6
SiMo ₁₂	2	+0.18	8.2	8	98 ± 6
P ₂ W ₁₂ Mo ₆	0.74	+0.05	3.7	3.52	95 ± 6

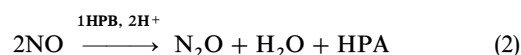
^a Solution: 5 ml of 0.2 M Na₂SO₄/H₂SO₄ (pH 1 solution) with C° of HPA. The reduction of each HPA is carried out on its first redox wave. For other details, see text. ^b Yield for the production of N₂O per mole of HPB. ^c Analysis and quantification by UV-visible spectroscopy.

potential shifts do not seem to reduce smoothly the catalytic efficiency. This strongly suggests that an intermediate adduct forms between HPA and NO. This finding is being elaborated on using a large variety of HPAs. Another point shows again that unsubstituted compounds, as well as the parent lacunary species, are active in this context. This was described in our patents^{1,2} for Keggin- as well as Dawson-type anions, and have recently been rediscovered and confirmed.^{4,6} Finally, we emphasize the case of multiply substituted HPAs, a new strategy initiated by our group,^{9,14} in which we study the substitution, in various locations of the W framework, by selected ensembles of identical or different heterometals. In this context, special emphasis will be put elsewhere on several examples not shown here and, in particular, on α₂FeP₂W₁₅Mo₂.

The results, in the following, are restricted to those HPAs for which the identification and quantification of the products of the catalytic process have been completed. The technique of mixing the reduced heteropolyanion with NO has been preferred here. It ensures that a homogeneous reaction proceeds cleanly, without any interference from the electrode potential and material on possible reaction intermediates and/or products. However, in the present case, its main advantage is to allow us to work with small volumes of HPB and pure NO, which is rather expensive. With such small-volume, tightly closed vessels, the determination of reaction yields on gaseous species is accurate. It has been checked, previously⁷ and in the present experiments, that continuous electrolysis of any of the selected HPAs in the presence of NO does give the same qualitative results. For quantitative measurements a larger volume, tightly closed electrochemical set-up, with NO bubbling, becomes necessary. Table 2 gathers the results. We have used combinations of several analytical techniques; in repeated experiments, N₂O was the only chemical detected. To complete the first reduction process observed in cyclic voltammetry for each HPA, either one or two electrons are required. As the same product is observed at the end of the reaction, we assume that one-electron-reduced HPAs proceed through the overall stoichiometry:



and that two-electron-reduced HPAs proceed through:



There is ample indication in the literature that the reduction of NO by one- and two-electron reductants yields mainly N₂O.^{15–17}

The yield for the generation of N₂O is then defined, following the two stoichiometries, as

$$Y = 100n \left(\frac{\text{moles of N}_2\text{O}}{\text{moles of reduced HPA}} \right)$$

with $n = 2$ and 1 , respectively, for one- and two-electron-reduced HPAs. The corresponding values are gathered in Table 2 and call for several comments. Handling gaseous species quantitatively requires particular care. Therefore, each result in Table 2 is the average of at least three replications of the same experiment. All the yields are close to 100%. The obtention of such high yields is also favoured by the relatively positive reduction potential of the present HPAs, the reduced forms of which are not or are hardly sensitive to residual oxygen in the electrolysis medium or to traces of oxygen that could enter the cell during the different stages of the experiments. It was checked by cyclic voltammetry and UV-visible spectroscopy that, in each experiment, the oxidized form of the HPA is fully regenerated after visual completion of the reaction, as indicated by the disappearance of the blue colour of the reduced oxometalates. The yields in Table 2 also seem to be independent of the reduction potential of the HPAs used in this work, thus reinforcing our previous mechanistic proposal of a “chemical catalysis” pathway. The detailed succession of electrochemical and chemical sequences occurring during this reaction is under investigation. For instance, the reduction of P₂Mo₁₈O₆₂^{6−} is a two-electron process, even in the absence of protons. The way in which P₂Mo₁₈O₆₂^{8−} delivers these two electrons to a substrate, simultaneously or in sequence, is an interesting problem.

In conclusion, Keggin- and Dawson-type heteropolyanions show catalytic behaviour for the reduction of NO in acidic aqueous media. This study was restricted to their first redox couples, for which the phenomenon is already visible. Unsubstituted and lacunary HPAs, as well as the substituted heteropolyanions of these two groups, prove active in this system. Five selected HPAs featuring one- and two-electron-reducible species were selected for further study in the present work. The only product detected in the reduction of NO is N₂O, obtained in quantitative yield, whatever the heteropolyanion. This work is interesting in its own right, but also constitutes a first step in a new strategy that consists in trying to accumulate several electrons on the first reduction waves of heteropolyanions, in order to study the electrochemical and chemical consequences of this multiple electronation possibility on the reaction products of the catalytic reduction of substrates like NO.

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