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Sonochemistry

Sonochemical Disproportionation of Carbon Monoxide in Water: Evidence for Treanor Effect during Multibubble Cavitation**

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Eighty years after the discovery of ultrasound-induced chemical processes,[1] known as sonochemistry, it remains a subject of extensive research.[2] It is generally accepted that sonochemistry arises from acoustic cavitation, which is the nucleation, growth, and implosive collapse of microbubbles in liquids subjected to ultrasonic waves. Nevertheless, debate still continues over the origin of extreme conditions created by the bubble collapse. Usually the sonochemical reactions are interpreted according to Flynn's "thermal" hypothesis presuming adiabatic or quasi-adiabatic transient heating of gases and vapours inside the cavitating bubble.[3] However, the recent observation of light emission from positively charged O_2^+ species during single-bubble collapse in H_2SO_4 provided evidence for nonthermal plasma formation inside the bubble.[4] The relationship between the mechanisms of single-bubble and multibubble cavitations is still not clear. Recent studies of multibubble sonoluminescence in H_2SO_4 and water revealed some similarities in the origin of both kinds of processes.[5,6] In this view thermal equilibration during the cavitation event remains an important question that is not yet resolved. Herein, we report the first "chemical" evidence for nonequilibrium molecule vibrational excitation occurring during multibubble cavitation.

We studied the ultrasonically driven disproportionation of carbon monoxide (DCO) in water saturated with a CO/Ar gas mixture. To our knowledge, this reaction had never been studied under ultrasonic irradiation. By contrast, the plasma–chemical DCO reaction in the gas phase has been a very active topic of research as working media for CO lasers and as a promising method for carbon isotope separation.[7] According to published results, the strongly endothermic DCO reaction ($\Delta H = 5.5\,\text{eV}\,\text{mol}^{-1}$, $E_a = 6\,\text{eV}\,\text{mol}^{-1}$) can be significantly accelerated by the vibrational excitation of CO molecules. The population of highly vibrational states $CO^*(\nu_n)$, $n \leq 40$, occurs through an anharmonic vibration-to-vibration pumping mechanism (V–V), known as the Treanor effect.[8] This approach produces nonthermal plasma far from the thermodynamic equilibrium with a vibrational temperature (T_v) of CO molecules much higher than their translational (T_0) or rotational (T_R) temperatures. An experimental illustration of the Treanor V–V pumping is a kinetic isotope effect (KIE) during DCO in nonequilibrium plasma.[9] The coefficient of isotopic selectivity (α) for vibrationally excited isotopes can be expressed by Equation (1), where $\frac{\Delta\omega}{\omega} = \frac{\omega_2 - \omega_1}{\omega_2}$ is the relative defect of resonance.[7]

$$\alpha = \exp\left[\frac{\Delta\omega}{\omega}E_a\left(\frac{1}{T_0} - \frac{1}{T_v}\right)\right] \qquad (1)$$

In quasi-equilibrium kinetics, light isotopes react faster because of their higher "zero vibration level" $\frac{1}{2}\hbar\omega$. In contrast, in nonequilibrium plasma, heavy isotopes react faster since they have higher vibrational temperature. Moreover, the nonequilibrium KIE is much stronger than the quasi-equilibrium effect.[7]

We found that the sonochemical DCO reaction exhibits some similarities with that in nonequilibrium plasma. At the same time, the sonochemical process includes not only the reactions in the gas phase, but also the secondary processes in a liquid phase whereby the products are formed inside the cavitating bubble. The sonication of water with 20 kHz ultrasound in the presence of CO/Ar gas mixture causes a drastic decrease in the H_2O_2 formation rate relative to that in pure Ar. The experimental details are presented in the Supporting Information. H_2O_2 is known to be a principal product of water sonolysis in the presence of noble gases.[1,2] Figure 1 demonstrates that only 10 mol% of CO is required to suppress completely the formation of H_2O_2. Furthermore, the pH value of water decreases with increasing CO concen-

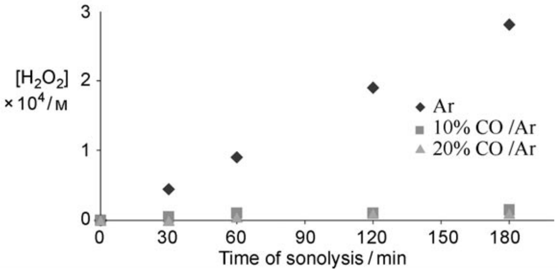

Figure 1. Kinetics curves of hydrogen peroxide sonochemical formation in water in the presence of Ar and CO/Ar gas mixtures. Initial pH value: 6.4; pH values after 6 h of sonolysis: 6.2 (Ar), 5.2 (10% CO/Ar), and 3.9 (20% CO/Ar). $f = 20$ kHz, $I = 27\,\text{W}\,\text{cm}^{-2}$, $P_{ac} = 0.60\,\text{W}\,\text{mL}^{-1}$, $T = 27$–$30\,°\text{C}$.

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tration, as shown in Figure 1. Sonication of water with pure argon does not lead to any significant acidification.

A simplified mechanism of water sonolysis in the presence of Ar is the homolytical splitting of water molecules as a result of the strong inelastic collisions inside the bubble followed by the mutual recombination of hydrogen atoms and $OH^{\bullet}$ radicals [Eqs. (2)–(6)].[10,11]

$$H_2O + Ar \rightarrow H_2O^* + Ar \tag{2}$$

$$H_2O^* \rightarrow H + OH \tag{3}$$

$$2\,H \rightarrow H_2 \tag{4}$$

$$2\,OH \rightarrow H_2O_2 \tag{5}$$

$$H + OH + M \rightarrow [H \cdots OH \cdots M] \rightarrow H_2O + M \tag{6}$$

In these equations, H_2O^* symbolizes the repulsive excited states of water molecule A^1B_1 ($E \approx 7.5$ eV) and B^1A_1 ($E \approx 8.3$ eV). The observed suppression of H_2O_2 formation as well as the acidification of water during sonolysis can thus be attributed to the scavenging of $OH^{\bullet}$ radicals by CO molecules inside the cavitating bubble [Eqs. (7) and (8)].

$$CO + OH \rightarrow CO_2 + H \tag{7}$$

$$CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^- \ (pK = 3.60)^{[12]} \tag{8}$$

Analysis of water sonicated for 6 h in the presence of a 20% CO/Ar mixture using electrospray ionization mass spectrometry (ESIMS) reveals the absence of organic acids ($\ll 10^{-4}$ M), such as HCOOH or $H_2C_2O_4$, which could be potential products of CO sonochemical oxidation in water. Therefore, it can be concluded that the acidification of water is mostly related to the formation of CO_2. Note that the solubility of Ar in water (1.3×10^{-3} mol kg^{-1} at 30 °C) is approximately twice than that of CO (7.1×10^{-4} mol kg^{-1} at 30 °C).[12] Consequently, for 10–20 mol% CO/Ar gas mixtures, the concentration of CO molecules inside the bubble should be significantly smaller than that of argon. It is therefore unlikely that the presence of CO would perturb the bubble collapse.

Another phenomenon that we observed during CO sonolysis is the formation of a solid, dark gray, carbon-containing product (CCP). This product can be removed from water by centrifugation after prolonged ultrasonic treatment. The TEM image (Figure 2) shows that the CCP consists of fine amorphous particles. The solid product also contains some relatively large irregular-shaped particles of titanium alloy originating from cavitation erosion of the ultrasonic probe (see Figure 1S in the Supporting Information). Roughly, only a few milligrams of CCP can be removed after 6 h of sonolysis with a 20% CO/Ar gas mixture. The presence of titanium particles and strong hydration of the solids made it difficult to obtain a precise value of the CCP yield. The amount of CCP formed during sonolysis was found to be very sensitive to the experimental conditions. Decreasing the CO concentration to 10% or heating the sonicated water to 45 °C resulted in a sharp decrease in CCP yield. Furthermore, no sonochemical reaction was observed with pure CO. The latter observation is in an agreement with the results of sonolysis of volatile organic compounds[10] and CO_2[13] indicating that a high intrabubble concentration of polyatomic molecules alters the cavitation event.

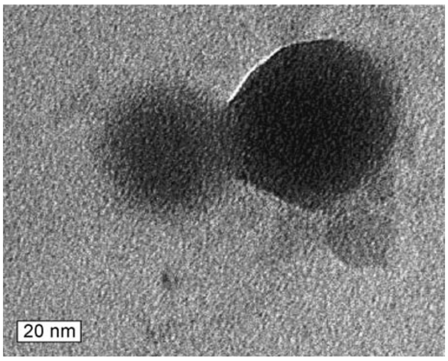

Figure 2. TEM image of the carbon-containing product formed during 20% CO/Ar sonolysis in water. A small amount of uranyl nitrate solution was added to the sample suspension in ethanol prior to deposition on a carbon-coated grid to improve the imaging contrast.

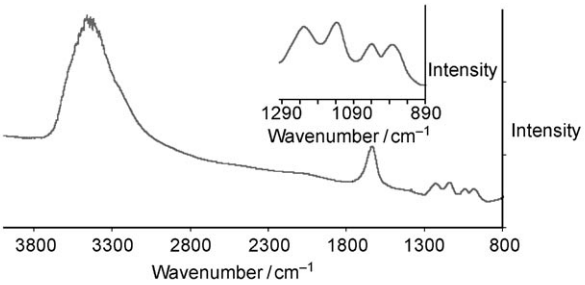

Figure 3. FTIR spectrum of the carbon-containing product formed during 20% CO/Ar sonolysis in water (KBr pellet).

Figure 3 shows the FTIR spectrum of the CCP. The strong band at around 3420 cm^{-1} is attributed to the stretching modes of H_2O molecules. The IR band around 1650 cm^{-1} could be assigned to the superposition of H_2O bending vibrations and the stretching modes of C=C and C=O bonds of anhydrides. The most interesting IR bands, in the range 1212–962 cm^{-1}, are shown in the inset of Figure 3. According to previously published data[14,15] the bands at 1225–1135 cm^{-1} and at 1036–978 cm^{-1} are related to (C=C)−O and (C=C)−C stretching vibrations, respectively, in poly(carbon suboxide) with a basic formula that can be represented as $(C_3O_2)_n$. This polymer has a polycyclic six-membered lactone structure. The FTIR spectrum of $(C_3O_2)_n$ under anhydrous conditions shows a band of the ketenyl group, C=C=O, at 2180 cm^{-1}.[15] However, exposure of the polymer to water results in the disappearance of this band. In our system, the absence of an absorption band at 2180 cm^{-1} in the FTIR spectrum of CCP also can be explained by hydrolysis of the ketenyl groups. The FTIR spectrum of CCP did not indicate the presence of either C−H (3000–2850 cm^{-1}) or COOH bonds (1710–1690 cm^{-1}). These data are in agreement with the results of ESIMS analysis, which revealed the lack of organic acids as the products of the sonochemical reaction.

Usually $(C_3O_2)_n$ polymer is formed during DCO in strongly nonequilibrium plasma [Eqs. (9)–(12)][9,16]

$$CO^*(\nu_1) + CO^*(\nu_2) \rightarrow CO_2 + C \tag{9}$$

$$C + CO(\nu_0) + Ar \rightarrow CCO + Ar \tag{10}$$

$$CCO + CO(\nu_0) + Ar \rightarrow C_3O_2 + Ar \tag{11}$$

$$n\,C_3O_2 \rightarrow (C_3O_2)_n \tag{12}$$

The similarity of the solid products for the sonochemical and plasma–chemical reactions allowed us to assume that the mechanism of ultrasonically driven disproportionation of CO is somewhat similar to that in nonequilibrium plasma. This hypothesis is fully confirmed by isotopic mass spectrometric analysis of carbon in the CCP. Table 1 reveals that the solid product of sonolysis is enriched with the ^{13}C isotope. The observed coefficient of isotopic selectivity was calculated as $\alpha = R_{\mathrm{exptl}}/R_{\mathrm{initial}}$, whereby $R = [^{13}C]/[^{12}C]$, presuming that only a small portion of CO accumulated inside the bubble is transformed into CCP during each collapse event. Table 1 also shows the estimated value of the equilibrium KIE for the DCO reaction calculated by using Bigeleisen–Mayer theory under the harmonic oscillator approximation {Eq. (13)},[17] where $u = \frac{hc\omega}{kT}$, $\omega_1 = 2078\ \mathrm{cm^{-1}}$, and $\omega_2 = 2125\ \mathrm{cm^{-1}}$ are the C–O stretching vibration frequencies for ^{13}C and ^{12}C, respectively, which have the strongest contributions to the reduced partition function ratio.[17]

Table 1: Experimental and calculated values of $^{13}C/^{12}C$ KIE (α) for carbon monoxide disproportionation.

System	δ [‰][a]	R [%]	α
initial 20% CO/Ar	−75.8	1.076	
after 6 h of sonolysis	−26.8	1.133	1.053
20% CO/Ar[b]	−25.1	1.135	1.055
calculated quasi-equilibrium KIE $2CO \rightarrow C + CO_2$[c]			ca. 0.995
non-equilibrium KIE in plasma			1.2–2.3[d] 3–5[e]

[a] The δ values were measured relative to PDB standard with a precision of 0.2 ‰ (see the Supporting Information). [b] Two parallel experiments. [c] Calculated using Equation (13), presuming its validity at $T = 4300$ K. [d] Glow discharge.[16,18] [e] Optical excitation.[9]

$$\alpha = \frac{u_1 \exp(-u_1/2)/\{1 - \exp(-u_1)\}}{u_2 \exp(-u_2/2)/\{1 - \exp(-u_2)\}} \tag{13}$$

For a gas temperature inside the cavitatiting bubble of about $T = 4300\ K$ according to a quasi-adiabatic heating model,[10] Equation (13) predicts a very small depletion of the solid product with the ^{13}C isotope. However, the experimental values of the KIE results demonstrate the enrichment of the CCP with a heavy isotope, which is in agreement with the Treanor V–V pumping mechanism. It can thus be concluded that the sonochemical disproportionation of CO cannot be interpreted as a process under thermal equilibrium. Consequently, this process is incompatible with the adiabatic heating model, which presumes the quasi-equilibrium state of gas inside the cavitating bubble.

Table 1 demonstrates that the observed value of α for the sonochemical reaction is lower than that for the DCO reaction in "conventional" nonequilibrium plasma. Probably, the observed KIE is decreased owing to the formation of the polymer $(C_3O_2)_n$. Equation (9) produces carbon enriched in ^{13}C isotope. In contrast, reactions of C and C_2O with unenriched CO would cause a decrease of the observed KIE in the final polymerized product. Slight variations in the experimental conditions, such as the temperature of sonicated water or the local gas concentration, would affect the composition of polymer. Such variations may explain the difference in the observed values of δ for two parallel experiments which exceeds statistical error. Another possible explanation of the rather low α value for the sonochemical process could be the relatively high translational temperature inside the cavitating bubble relative to that in nonequilibrium plasma generated by glow discharge or laser irradiation. A survey of recent literature showed that the nonequilibrium excitation of CO molecules might be attained in the high temperature reacting gas flows usually behind the shock wave front.[19] Shock wave emission with a velocity of about $4000\ \mathrm{m\,s^{-1}}$ from a sonoluminescing bubble has been proven experimentally.[20,21] The nonequilibrium chemical processes behind strong shock waves are demonstrated to occur predominantly through non-collinear collisions with simultaneous transfer of rotational and translational energy to the vibrational mode of the dissociating molecule.[19] Inside the cavitating bubble, the vibrational excitation of CO molecules would occur by collisions with Ar or H atoms in the reactive gas behind the shock front created during bubble collapse [Eqs. (14) and (15)].

$$CO(\nu_0) + Ar \rightarrow CO(\nu_n) + Ar \tag{14}$$

$$CO(\nu_0) + H \rightleftharpoons (HCO) \rightarrow CO(\nu_n) + H \tag{15}$$

The cross section of CO vibrational excitation by collisions with H atoms is known to be higher than that for collisions with Ar atoms.[22] Therefore, Equation (15) can play an important role in CO vibrational excitation even if the intrabubble H atom concentration is less than that of Ar. In principle, whatever the reaction that caused CO excitation, the observed Treanor effect clearly indicates that the vibrational temperature of CO molecules inside the cavitating bubble is higher than the temperature of translational degrees of freedom of molecules. However, further work will be needed to understand the details of the vibrationally excitation during the acoustic collapse. Particularly, it would be of great interest to investigate whether the charged species are formed during multibubble cavitation.

In conclusion, we have found that the solid carbon-containing product formed during water sonolysis with 20 kHz ultrasound in the presence of CO/Ar gas mixture is enriched with ^{13}C isotope ($\alpha = 1.053$–1.055). Such a kinetic isotope effect provides a convincing argument for the formation of vibrationally excited CO molecules with a nonequilibrium Treanor distribution ($T_v > T_0$) inside the cavitating bubble. It was found the solid product of sonolysis contains the hydrated polymer of carbon suboxide $(C_3O_2)_n$, confirming some similarities between sonochemical and plasma–chemical processes. The lack of thermal equilibrium during acoustic collapse is inconsistent with the currently dominated model of multibubble sonochemistry based on adiabatic heating approach.

We expect that the nonequilibrium approach offers some new implications for sonochemical reactions in general. Processes away from thermal equilibrium often have significant advantages over the thermally equilibrated systems, because they require much less energy and provide high conversion degree and high selectivity.

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