TABLE VII: Symmetry Force Constants (mdyn/A) for FC	BLE VII	Symmetry Force	Constants (mdvn/Å)	for FON	Ň
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	1	2	3	4	5	6
			LDF Cis	3		
1	13.02					
2	1.38	9.29				
3	0.23	1.03	1.95			
4	0.46	1.14	-0.53	1.12		
5	-0.09	-0.48	0.16	-0.25	0.57	
6						0.23
			LDF Trai	ns		
1	12.78					
2	0.55	14.34				
3	0.40	0.14	1.08			
4	0.51	0.85	-0.09	0.19		
5	-0.16	0.11	0.16	-0.09	0.48	
6						0.09

Experimental, Using Cis Frequencies and Trans Configuration and Assuming $\nu_5 = 205 \text{ cm}^{-1}$ (refs 4, 5)^a

13.06				
2.52	8.48			
0	0	1.01		
0.90	-0.27	0.43	1.32	
0	0	0	0	0.30
	13.06 2.52 0 0.90 0	13.06 2.52 8.48 0 0 0.90 -0.27 0 0	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$

^a In the "experimental" force field, the deformation and stretch-bend interaction constants have been normalized for distance and have dimensions of mdyn Å rad⁻² and mdyn rad⁻¹, respectively.

predicted (166 cm⁻¹) is below the spectrometer cutoff of the previous experimental study⁴ and, therefore, would not have been observed. Thus, the calculations for *cis*-FONO can account for all the observed features, and the approximate mode descriptions previously given⁵ by Sorenson and Noble are correct, although made for the incorrect trans isomer. In view of the ab initio CISD/6-31G* calculations failing to yield a correct geometry for FONO (see above), it is also not surprising that they could not reproduce³ the experimentally observed frequencies.

The force constants calculated by the LDF method for *cis*- and *trans*-FONO are given in Table VII and are compared to the force

field previously reported⁵ for *trans*-FONO using the experimental⁴ *cis*-FONO frequencies and isotopic shifts for $\nu_1 - \nu_4$ and assuming a frequency of 205 cm⁻¹ for ν_5 . In spite of the obvious shortcomings of this "experimental" force field, it can be seen that it agrees much better with the LDF cis-isomer force field than with the trans-isomer one. This lends further support to our conviction that the previously reported infrared spectrum must be due to the cis and not to the trans isomer of FONO.

The force field of cis-FONO (see Table VII) is in good agreement with our expectations¹ for such a molecule. It shows significant coupling between the two NO stretches and between the internal N-O1 stretch and the O-F stretch and ONO scissoring mode. The suggested large difference of 3.73 mdyn/Å between the two N-O stretching force constants is somewhat surprising in view of their relatively small difference in bond lengths of only 0.026 Å. This force constant difference strongly depends on the values of the interaction force constants which are quite large in FONO. The calculated LDF force field and geometry, together with the available experimental isotopic shifts,⁴ could be used to fine tune the force field and to verify the large difference in the N-O stretching force constants. This large difference could be caused by strong perturbations in the electronic structure of the ONO fragment of FONO due to the weakly bonded fluorine atom.

Conclusion

The LDF method is well suited for the prediction of the structures and vibrational spectra of "problem" compounds such as FOOF and FONO for which conventional ab initio molecular orbital methods at the CISD/6-31G* level fail. Furthermore, the vibrational spectra previously reported⁴ for FONO and attributed to its trans isomer are compatible only with the cis isomer. The bonding in *cis*-FONO resembles that in FOOF and consists of a fluoride ligand loosely coupled through an oxygen atom to the NO₂ molecule, thus resulting in weak F–O and strong NO₂ bonds.

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Forced Electrochemical Nonlinear Oscillator Assembled on Rotating Ring–Disk Electrodes

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Self-sustained potential oscillation was observed on a polycrystalline platinum ring electrode under the galvanostatic (constant current) electrochemical oxidation of formaldehyde in a rotating ring-disk electrode cell. When a pulsed stream of hydrogen was supplied to the ring electrode from the disk electrode, the self-sustained oscillation changed to the forced oscillation under certain conditions.

Introduction

Some chemical reactions oscillate. The Belousov–Zhabotinski reaction is famous along oscillating homogeneous reactions.¹ In heterogeneous reactions, the catalytic oxidation of carbon mon-

oxide on the platinum surface is an established oscillating reaction.^{2,3} Recently, instabilities in electrochemical systems have attracted great interest.⁴⁻⁹ Some of them show transition into

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chaos^{4,6} and bifurcation sequence in mixed-mode oscillatory states.5,6

Forced and coupled systems of nonlinear chemical oscillators are common in living organisms. The forced system is exemplified by the temporal evolution of cardiac rhythms periodically forced by cardiac pacemakers¹⁰ and the coupled system by the mutual interference of neural oscillators in the brain.^{11,12} However, artificial counterparts of such systems have hardly been constructed. This article demonstrates that a chemical system in which forced oscillations are caused by the modulation with the concentration wave of a chemical substance is simply assembled by coupling electrochemical reactions by using a rotating ring-disk electrode (RRDE).13

The instability of electrochemical systems is generally ascribed to apparent negative resistance due to the passivation of electrode reactions,^{14,15} which is caused (1) by the formation of the oxide layer as often seen in the anodic oxidation of metal electrodes^{4-6,14,15} and/or (2) by the strongly adsorbed electrochemically inert species as occurs in the oxidation of small organic molecules.⁷⁻⁹ The interaction of a self-sustained electrochemical oscillation with another electrochemical reaction requires a chemical species common to both the reactions.

In this study using the RRDE, self-sustained oscillations of the electrode potential were provided by the galvanostatic oxidation of formaldehyde on the platinum ring electrode. The forced oscillation was induced by the hydrogen pulse supplied by periodical potentiostatic reduction of water on the platinum disk electrode.¹⁶ Hydrogen molecules formed on the disk are efficiently transferred to the ring in hydrodynamic laminar flow.

Experimental Section

A Nikko-Keisoku RRDE system was used. It consists of a DPGS-5 dual potentiogalvanostat, an NPS-2 potential sweeper, an SC-5 motor-speed controller, and an RRDE-1 mechanical driving unit. The potential and current signals were recorded on a LeCroy 9400 dual digital oscilloscope and plotted on a Hewlett-Packard HP 7475A plotter.

The electrochemical cell was temperature controlled by a circulating thermostatic bath, NesLab RTE-5B. The reference and the counter electrodes were a TDA HC-205C saturated calomel electrode and a 15-cm platinum wire, respectively. The RRDE consisted of a platinum disk of 5.5 mm in diameter and a platinum ring 6.5 and 9 mm in inner and outer diameters, respectively.

Electrolyte solution was freshly prepared aqueous solution containing 0.4 M formaldehyde and 2.0 M sulfuric acid. Temperature was kept constant at 323 K in all the experiments. Before each experiment, the surface of the electrode was polished with diamond paste on a Kulzer-Technotron polishing disk and rinsed with distilled water. The platinum ring electrode was electro-chemically activated by Schell's method:⁷ repeating 10 cycles of a potential sequence of holding for 1 min at 2.0 V followed by -0.4 V for 10 s.

The ring-disk electrode was rotated at 4000 rpm. Dissolved oxygen was purged by bubbling with nitrogen. The self-sustained oscillation of the ring-electrode potential was initiated by slowly



Figure 1. The response of the ring-potential oscillation to the disk-current pulse on an RRDE. Ring current: galvanostatic at 250 µA. Disk potential: swept up and down alternatively at a rate of 2 s V^{-1} between -0.4 and +0.1 V.

increasing the galvanostatic anodic current. The potential of the disk electrode was modulated with a triangular wave between a voltage for hydrogen evolution and one for nil current, -0.4 and +0.1 V vs SCE, respectively.

Results

The ring-potential oscillation was successfully initiated in ca. 90% of the experimental runs. Its amplitude centered on 0.4-0.5 V vs SCE. Its period and wave form depended mainly on the current but also on various factors including unknown and uncontrollable ones. Durations of the self-sustained oscillation scattered from 1 to 60 min. This paper describes the results of experiments in which the oscillation lasted more than 10 min.

When the self-sustained oscillation ceases, the amplitude decreases with the period disturbed, and finally the potential rises to converge to a value of ca. 1 V for a stationary state. Oscillations can be reinitiated by resetting the current to zero followed by increasing it gradually. The duration of the reinitiated oscillation was similar to the preceding one. This similarity suggests that the surface conditions mainly govern the duration in our experiments. The reinitiation was difficult when the current was directly decreased from the high stationary potential. There seems to be a supercritical bifurcation point which should be passed from the low to high current to come into oscillation.

The disk electrode was driven by a triangular voltage wave. The disk current due to the hydrogen formation was a sharp pulse wave with the same interval as the driving wave. The pulse represents the change in the hydrogen concentration which modulates the oscillating oxidation reaction on the ring electrode.

A sequence from a self-sustained oscillation (region I) to a forced one (region III) via a transient region (II) is shown in Figure 1, which depicts the oscillations in the ring-electrode potential and in the disk-electrode current. Both the wave form and the period of the ring-electrode potential differ between the self-sustained and the forced oscillations. The presence of the transient region and the change in period and wave form are characteristic of forced nonlinear oscillators.^{17,18}

Figure 2 shows forced oscillations for interfering hydrogen pulses of different intervals. It also shows that the self-sustained oscillation recovers without a marked transition region when the interfering pulse stops. The wave form of the forced oscillation differs markedly from that of the self-sustained one in (b) and (c) but little in (a) in Figure 2. The wave form of the forced oscillation never fit the superposition in the wave form of the interfering pulse on the self-sustained oscillation.

Detailed correspondence between a forced oscillation and an interfering pulse series is illustrated in Figure 3. The interference

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Figure 2. Forced oscillations for hydrogen-pulse intervals of (a) 0.1, (b) 0.2, and (c) 0.3 s at a ring current of 100 μ A.



Figure 3. A part of Figure 2c expanded demonstrating the modulation of the ring-potential oscillation by the disk current pulse.

added positive bumps to the original oscillation.¹⁹ The wave form as well as the period of the forced oscillation depended not only on the interval of the interefering pulses but also on the phase difference between the original oscillation and the interfering pulse. In the particular example shown in Figure 3, there are three seemingly different patterns of interference as denoted by α , β , and γ . As shown in Figure 2, the fine structure of the forced



Figure 4. A scheme for the self-sustained potential oscillation (solid arrows) and for processes of the interference of hydrogen (dotted arrow).

oscillation tends to become complicated as the interval of the interference pulse decreases but becomes smooth if the interval is too small.

Discussion

Discussion will be limited to chemical reactions that may be involved in the observed oscillations, although there is another approach by phenomenological simulations based on the Franck-FitzHugh equation.^{14,15}

A scheme presented in Figure 4 seems reasonable for the observed self-sustained and forced oscillations according to the present knowledge concerning the catalytic and electrochemical oxidation of formaldehyde, formic acid, and methanol.²⁰⁻²³

The self-sustained potential oscillation can be explained qualitatively as follows. The electrochemical oxidation of formaldehyde on platinum electrode proceeds through a direct path and an indirect path where the adsorbed formaldehyde is converted to carbon monoxide adsorbed on the surface, Pt-CO.²⁴ This carbon monoxide passivates the electrode reaction. The passivation shifts the electrode potential toward positive to keep the galvanostatic condition by accelerating the direct-path reactions. When the electrode voltage becomes anodic enough to form the adsorbed hydroxide, Pt-OH, the adsorbed carbon monoxide is removed by

$$Pt-CO + Pt-OH \rightarrow 2Pt + CO_2 + H^+ + e^-$$

The resultant recovery of the active platinum site shifts the electrode potential toward negative.

There are two possible processes on which hydrogen can interfere to lead to forced oscillation, as shown by dotted arrows in Figure 4. In process A, hydrogen decreases Pt-OH to increase the carbon monoxide. In process B, hydrogen converts an oxidized species (Pt-COOH) to the carbon monoxide. The increase in the carbon monoxide concentration shifts the electrode potential toward positive. Thus, the observed positive bumps in the forced oscillation are explained.

The detailed analysis including the numerical simulation of the reaction dynamics as well as the identification of the reaction intermediate is in progress.

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