The Journal of Physical Chemistry

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VOLUME 95, NUMBER 15 JULY 25, 1991

LETTERS

ESR Studies of the Oscillations of the Malonyl Radical in the Belousov–Zhabotinsky Reaction in a CSTR

B. Venkataraman*,[†] and P. Graae Sørensen

Department of Chemistry, H.C. Ørsted Institute, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen, Denmark (Received: March 15, 1991; In Final Form: May 29, 1991)

Electron spin resonance studies of the malonyl radical, formed during the Beluosov-Zhabotinski reaction with bromate, Ce^{4+} , and malonic acid, have established that the concentration of the free radical also undergoes oscillations. The free radical closely follows the Ce^{4+} . In a CSTR, when bursts occur at certain flux rates, the free radical also exhibits burstlike behavior. However, when the oscillations of the free radical is quenched by passing oxygen through the system the bromide ion and Ce^{4+} continue to oscillate, thereby casting doubt on the recent suggestion that the free-radical pathway is an important route for the control of the oscillations.

Introduction

In spite of several years of investigations, the role of malonyl radical is not well understood in the classical variant of the Belousov-Zhabotinski reaction where malonic acid (MA) is oxidized by acidic bromate in the presence of a cerium catalyst. In a new model, called the Radicalator model, a suggestion has been made that an additional feedback loop based on the reaction of the malonyl radical with BrO2* plays a major role in the control of the oscillations.¹ We have followed the variation of the concentration of the malonyl radical utilizing the electron spin resonance technique, as the system starts oscillating after an induction period and during burst oscillations that can be induced in a CSTR at sufficiently high flow rates. We have established that the concentration of the malonyl radical also undergoes periodic oscillations and have determined the phase of the oscillation of the malonyl radical concentration with respect to the oscillations of the Br⁻ and Ce⁴⁺. The effect of oxygen, either present in the

[†]Permanent address: Tata Institute of Fundamental Research, Homi Bhabha Road, Bombay 400005, India. solutions at the start or forcibly inducted at different stages, was examined.

The ESR detection of malonyl radicals in a flow system of Ce⁴⁺/MA was reported by Amjad et al. and Brusa et al.,² and the effect of the addition of HBrO₂ to this system was studied by Försterling et al.¹ The malonyl radical has a doublet ESR spectrum with g = 2.0037 and $a_{H}^{\alpha} = 2.03 \pm 0.03$ mT. All our investigations on the time dependence were carried out on the low-field line with the exception of one set of experiments, which was carried out on the high-field line to confirm that its time dependence is identical with that of the low-field line.

Experimental Section

The ESR measurements were carried out in a Bruker ESP300 ESR spectrometer. For initial measurements, 0.2 M MA in 1

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Figure 1. Schematic representation of the experimental arrangement used to follow simultaneously the variation in the concentrations of Br⁻, Ce⁴⁺, and malonyl radical in a CSTR. Reservoir 1 contained 0.1 M KBrO₃ in 1.5 M sulfuric acid. Reservoir 2 contained 0.25 M malonic acid and 0.0005 M Ce₂(SO₄)₃ in 1.5 M sulfuric acid. The outputs 1, 2, and 3 that measure [Br⁻], [Ce⁴⁺], and [malonyl radical], respectively, are fed to three analog channels of a microcomputer and sampled separately and sequentially with an interval of 0.2 s.

M sulfuric acid and 0.002 M Ce(SO₄)₂ in 1 M sulfuric acid were mixed together in a quartz liquid flow mixing chamber and reaction ESR cell (type WG-804 of Wilmad Glass Co., Buena, NJ) and the ESR spectrum of malonyl radicals was investigated at different flow rates through the cell. The flow was controlled with a Cole-Parmer Model 7521-10 peristaltic pump with a two-component mixing head. The sample cell was placed in an X-band homemade rectangular TE₁₀₂ cavity, with modifications of the narrow dimensions of the cavity to accommodate two single-turn parallel modulation coils placed inside the cavity. By an appropriate impedance matching network it was possible to achieve a 100-kHz magnetic field modulation of 1 mT peak-to-peak with the power amplifier provided in the Bruker spectrometer. The modulation depth was calibrated in the usual manner with a small amount of solid DPPH. The spectra and the concentration of the free radical agree well with the findings of Försterling and Noszticzius.¹ Using 10⁻⁶ M aqueous solution of 4-hydroxytempo as a standard, we estimate the concentration of the malonyl radical in this experiment and in experiments described below.

To determine whether the malonyl radical concentration oscillated in a typical BZ reaction mixture, the experiments were conducted initially in a closed system where the reactants (1 M MA, 0.002 M Ce³⁺, and 0.2 M KBrO₃ in 1.5 M sulfuric acid) were all mixed in a reactor with a volume of 150 mL, which was constantly stirred. Nitrogen gas was bubbled into the solution in the reactor and the solutions were also flushed with nitrogen before mixing. The oscillations in the reactant mixture were followed with a Radiometer Br- ion selective electrode. The reactant mixture was flowed into a flat quartz flow type ESR cell (type WG-814, Wilmad Glass Co.) by the peristaltic Cole-Parmer pump and returned to the reactor. The output of the 100-kHz phase-sensitive detector, with the magnetic field set at the position of maximum positive signal, was fed to a strip-chart recorder and to one of the channels of the data acquisition system to be described later. The microwave power and the field modulation amplitudes were changed, and the effect on the oscillations was studied. To ensure adequate sensitivity, 31-mW microwave power and a modulation depth of 0.18 mT were employed, and the time constant was 5.2 s. These values were chosen after ensuring that in this range the time dependence of the ESR signal reflected truly the time dependence of the concentration of the malonyl radical. Flow rates through the ESR sample cell were varied from 27 to 58 mL/min, and it was observed that the periodicity of the ESR signal matched with the periodicity of the Br⁻ electrode potential at all these flow rates. However, the periodicity of the oscillations exhibited variations with the flow rate, but the fact that both the periodicities matched each other confirms that the system in the reactor cell and the ESR sample cell system together form parts of a complete homogeneous system for the flow rates employed. The malonyl radical concentration was estimated to be below 30 nM in all the studies reported here and the oscillations occur presumably between this concentration and nearly zero concentration.

The second set of experiments were conducted in a CSTR, where the periodicity of oscillations was controlled by the flow rate of the reactants through the reactor. The flow rates were controlled by a peristaltic pump (Ismatec Model IP-4), which controlled both the inflow and outflow of the reactants. The first reactant consisted of 0.1 M KBrO₃ in 1.5 M sulfuric acid and the second was 0.25 M MA and 0.0005 M $Ce_2(SO_4)_3$ in 1.5 M sulfuric acid. The mixture consists of equal volumes of the two solutions, and hence the active concentrations are halved. At fast flow rates the system is known to exhibit bursts in oscillations. In this set of experiments the changes in the Ce⁴⁺ concentration was also followed photometrically by measuring the light absorption from an incandescent lamp at 350 nm. The reaction cell was made of Plexiglass with rectangular faces. The volume of the fluid in the cell was kept constant at 150 cm³. Figure 1 is a schematic representation of the experimental arrangement. The reactant mixture is flowed through the ESR sample cell with the auxiliary Cole-Parmer pump and returned to the reactor. Here again it is established, by comparing the periodicities of the ESR signal, bromide electrode potential, and Ce4+ optical absorption, that the reactants in the ESR sample tube and the reactor have similar temporal behavior only when the system is oscillating steadily (Figure 2). When bursts occur at faster flux rates through the reactor, the ESR signal shows a temporal behaviour different from those of Br⁻ and Ce⁴⁺ during the quiescent periods. Further investigations, wherein the Ce4+ concentrations in the reactor and the ESR sample cell were followed simultaneously, revealed that only during the steady oscillating state the time variations of the Ce⁴⁺ concentrations in the two systems followed each other closely.



Figure 2. Variation of Br^- , (1), malonyl radical (MA^{*}) (2), and Ce⁴⁺ (3) concentrations with time in a CSTR: (A) the steady oscillation state; (B) the condition where bursts occur. Note that a decrease in mV in (1) corresponds to an increase of [Br⁻] and that an increase of mV in (2) and (3) corresponds to an increase of [MA^{*}] and [Ce⁴⁺] respectively. In this figure and the following ones, the t in the X axis corresponds to time in seconds.



Figure 3. Variations of Ce⁴⁺ with time in the flat ESR cell (2) and the CSTR reactor (1) (A) during the steady oscillatory state and (B) the state when bursts occur. The concentrations of Ce⁴⁺ are measured spectrophotometrically at both the sites.

During quiescent periods of the bursts there was no match between the changes in the two systems (Figure 3). These findings are understood when it is realized that the onset of bursts, periodicity, etc., depend critically on flux rates as well as mechanical disturbances, and apparently the conditions in the two systems are not strictly identical, leading to differences in behavior when the system is very unstable.

The data acquisition was controlled by a microcomputer equipped with a 13-bit A/D converter. The three analog channels corresponding to Br^- , Ce^{4+} , and malonyl radical were sampled separately and sequentially with an interval of 0.2 s, and the data were stored separately for future processing. **Materials.** Sulfuric acid (H_2SO_4 , Merck, 95–97% p.a.) was diluted to 1.5 M with doubly distilled water. Potassium bromate (KBrO₃, Merck, p.a.) was dissolved in 1.5 M H_2SO_4 . Malonic acid (MA, Aldrich, p.a.) was recrystallized from acetone-chloroform and finally dissolved together with cerium(III) sulfate (Ce₂(SO₄)₃, Morton Thiokol, 99.9%) in 1.5 M H_2SO_4 . Pure nitrogen gas was obtained by boiling off liquid nitrogen.

Results and Discussion

Start of Oscillations in a Closed System. It is found that the time dependence of the concentration of the malonyl radical in the flat ESR cell does not follow a predictable pattern at the start



Figure 4. Variation of Br⁻ in the CSTR and malonyl radical (MA[•]) in the ESR cell at two different flow rates through the ESR cell while maintaining the flux of the reactants in the CSTR constant; flow rate through the ESR cell is 34 mL min⁻¹ for (A) and 49 mL min⁻¹ for (B).



Figure 5. Variations of the concentrations of the three species during bursts in a CSTR: (A) low flux rate through the CSTR; (B) higher flux rate, when bursts occur more often.

of the reaction and it takes a few cycles before the three oscillations monitored fall in step with one another. The pattern at the start varies from run to run and also depends on whether the solutions making up the reactant system had been flushed with nitrogen before start or not. As pointed out earlier, we can correlate concentrations in the flat ESR cell with those in the reactor only after the onset of the steady oscillatory condition. However, it is noted that the concentration of the radical starts high at the beginning (about 1.8×10^{-8} M) and decreases on the onset of the oscillation. Saturation of both the solutions with oxygen before mixing prevents the ESR signal from being observed at the start. However the oscillations of Ce^{4+} and Br^- are observed, and during the beginning of these oscillations there are some small amplitude oscillations of the ESR signal; it is clear that oxygen does not scavenge all the free radicals.

Simple Limit Cycle Oscillations. Figure 4 shows two sets of data for different flow rates through the ESR flat cell, and from these we infer that under the steady oscillatory condition the system in the flat cell is homogeneous with the system in the reactor and that the radical concentration follows that of Ce^{4+} . That the radical concentration follows the Ce^{4+} concentration is established by the following observations: (i) By enlarging the



Figure 6. Effect of passing oxygen through the reactor at the point marked on the ESR spectrum (2). Note that even though oscillations have stopped for (MA*) on passing oxygen, the free-radical concentration remains high.

curves in Figure 2A, it is found that the periodicities of all the oscillations are identical and that the temporal behaviour of the ESR signal closely follows that of the Ce^{4+} concentration. (ii) The fact that we see unusual behavior of the ESR signals in the ESR flat cell during the quiescent periods in bursts, similar to those found for the Ce⁴⁺ optical absorption (Figure 3B) in the ESR cell, under similar circumstances, enforces this inference. (iii) On enlargement of the three curves of Figure 2A and comparing the resulting traces with the enlargements of the two curves of Figure 3A it is found that the temporal behavior of [Br-] and [Ce⁴⁺] is in conformity with what has been observed and accounted for earlier.³ A rapid rise of [Br⁻] is followed by a relatively slower fall of [Ce⁴⁺] and the slower fall in [Br⁻] is followed by a rapid rise in [Ce⁴⁺]. By comparing the two traces in Figure 3A it is seen that while the rapid fall of $[Ce^{4+}]$ is similar in both the cells the slower rising part of $[Ce^{4+}]$ seems to be slower in the ESR flat cell. What is observed for the ESR signal of malonyl radical also has a slow rising part and a rapidly decreasing part almost concomitant with the behavior of [Ce4+]. It is still unclear whether there is a definite time lag between the rise and fall of the Ce⁴⁺ concentration and that of the malonyl radical.

Burst Oscillations. Two typical sets of data are presented in Figure 5. It is clear that the radical concentration also exhibits similar behavior, but we should not attempt to correlate the three



Figure 7. Effect of passing oxygen under conditions of rapid bursts with a high flux rate through the CSTR; the ESR signal shows small amplitude oscillations even in the presence of oxygen.

concentrations during the quiescent period of the burst or at the start of an oscillatory behavior after a quiescent period.

Effect of Passing Oxygen. To determine the role of the free radical in the control of the oscillatory behavior, the reactant mixture was flushed with oxygen in different ways and the subsequent effects investigated. If, during the middle of a steady oscillatory state in a CSTR, oxygen is injected into the reactor, as in Figure 6, the oscillations of the malonyl radical stop while that of Ce⁴⁺ and Br⁻ continue. It may be argued that oxygen may broaden the ESR spectrum of the malonyl radical significantly, to prevent its detection at the low concentrations prevalent in this system. However, the level of the ESR signal does not fall to zero on passing oxygen, suggesting that the broadening effect is insufficient to prevent detection of the ESR signal. It is also surprising that while the oscillations are mostly quenched, the concentration of the free radical remains at a higher value. This implies that the production of the radical by Ce⁴⁺, is at a faster rate than the rate of scavenging by the oxygen at the flow rates employed. At high flux rates through the reactor, when bursts are frequent, the ESR signal due to the malonyl radical continues to oscillate, but with a lower amplitude, even when oxygen is bubbled, as shown in Figure 7. If the solutions are saturated with oxygen before mixing in the reactor of a closed system, no oscillations are detectable, except at the beginning and end of the oscillatory period of Ce4+ and Br-. The observation that in all the cases where oxygen is bubbled into the system, there is no drastic change in the oscillations of the Ce⁴⁺ and Br⁻, even when the oscillations in the malonyl radical concentrations is absent or

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very low in amplitude, casts doubt on the suggestion that the free-radical pathway is the most important route for the control of the oscillations.

It is not possible to propose a model for the findings reported here, until more careful measurements are carried out with different concentrations of the reactants.

Acknowledgment. We thank Ms. Merete Torpe for help in carrying out the measurements and Dr. Erik Pedersen for collaboration and assistance in the ESR instrumentation. B.V. expresses his thanks to the Danish Research Academy and Professor Thor A. Bak for making it possible to avail of a visiting professorship at the Ørsted Institute.

Ultrafast Measurements on Direct Photoinduced Electron Transfer in a Mixed-Valence Complex

Gilbert C. Walker, Paul F. Barbara,*

Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

Stephen K. Doorn, Yuhua Dong, and Joseph T. Hupp

Department of Chemistry, Northwestern University, Evanston, Illinois 60208 (Received: May 1, 1991; In Final Form: June 6, 1991)

A direct measurement of the kinetics of intramolecular photoinduced metal-metal charge transfer has been made, i.e.

 $(NH_3)_5Ru^{III}NCFe^{II}(CN)_5 \xrightarrow{h\nu}_{k_{ET}} (NH_3)_5Ru^{II}NCFe^{III}(CN)_5$

where the solvent is H_2O or D_2O and k_{ET} signifies the reverse-electron-transfer (ET) rate coefficient. The apparent reverse-electron-transfer kinetics are nonexponential with a limiting rate constant, $k_{lim} = k(t)$ where $t \to \infty$, equal to (8 ± $3) \times 10^{11}$ s⁻¹. This is close to the theoretical predictions from the model of Sumi and Marcus (classical vibrational modes), $k_{\text{ET,SM}} = 10^{13}$ and 5×10^{12} s⁻¹, and from the model of Jortner and Bixon (quantum mechanical vibrations), $k_{\text{ET,JB}} = 1.2 \times 10^{12}$ s⁻¹. The parameters required for these theories were estimated by resonance Raman spectroscopy, static absorption spectroscopy, and recently published transient Stokes shift measurements.

Introduction

Compounds exhibiting mixed-valence metal-metal chargetransfer transitions (MMCT)¹ have played a central role in the development of the understanding of electron-transfer (ET) reactions. In Marcus's theory of ET,² the energy of the absorption maximum $h\nu_{max}$ gives direct information on the reorganization energy λ , as follows

$$h\nu_{\max} = \lambda + \Delta G^{\circ} \tag{1}$$

where h is Planck's constant and ΔG° is the driving force, as shown in Figure 1, which represents the reaction described in this paper.

The MMCT absorption band also gives a measure of a key ET parameter, the electronic matrix element, V_{el}^{3} Resonance Raman spectroscopy on the MMCT band gives detailed information on the vibrational modes that are coupled to the ET reaction.⁴ Two additional types of data are needed for an "absolute" rate prediction, namely, a measure of the dynamics of the solvent coordinate and a measure of the reaction driving force ΔG° . For a typical MMCT compound, such as in Figure 1, ΔG° can be approximately estimated from redox potential of the isolated metal systems or other methods. Estimates for the required solvation dynamical information are available from recent transient Stokes shift measurements on polar fluorescent probes.⁵ In summary, all the parameters that are necessary to make a prediction of the ET rate constant, $k_{\rm ET}$, for MMCT compounds can be experimentally obtained, but no such comparison has been reported to our knowledge.

In this paper, we report the first direct kinetic measurement of a MMCT optically induced ET reaction, as represented in Figure 1, and compare the experimental results to theoretical predictions using experimentally estimated parameters. It should be noted that a report has appeared in which MMCT kinetics were indirectly induced by metal-ligand charge-transfer optical excitation.⁶ Our work is oriented, in part, toward evaluating contemporary theoretical models that explicitly consider the dramatic effect of solvation dynamics on ET rates.⁷ In the past decade it has been established that ET rates can be directly proportional to the time scale for solvent motion for simple systems in certain limits, i.e.

$$k_{\rm ET} \simeq \tau_{\rm s}^{-1} \exp(-\Delta G/k_{\rm b}T)$$
 (2)

Thus for small barrier reactions ($\Delta G \ll k_b T$) $k_{\rm ET}$ is solvent controlled, i.e., $k_{\rm ET} \simeq \tau_s^{-1}$. We are particularly concerned in this paper with obtaining experimental evidence on how the simple picture of eq 2 is affected by strong electronic coupling, vibrational modes, and frequency-dependent solvent friction effects.⁷

Experimental Methods

The transient pump-probe apparatus has been described elsewhere.⁸ The laser source is an intermediate repetition rate (8.2 kHz) amplified dye laser ($\lambda = 792$ nm) with 70-fs pulse duration. The energies of the pump and probe pulses were typically 400 and 20 nJ, respectively. The spot sizes were $\simeq 100 \,\mu m$. The continuum light probe pulses were generated in water or a

^{*} To whom correspondence should be addressed.

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