

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231407586>

Estimation of the rate constant of the $\text{Ag}^+ + \text{Br}^-$ reaction. The possibility of non-bromide-controlled oscillations in the Belousov-Zhabotinskii reaction

ARTICLE in THE JOURNAL OF PHYSICAL CHEMISTRY · JANUARY 1988

Impact Factor: 2.78 · DOI: 10.1021/j100313a027

CITATIONS

10

READS

20

2 AUTHORS, INCLUDING:



Zoltan Noszticzius

Budapest University of Technology and Econ...

99 PUBLICATIONS 1,892 CITATIONS

SEE PROFILE

The summation over v in (A17) is taken up to the dissociation limit of $H_2(X)$.

Case 4. In this case, one considers the process in case 3 except for the additional assumption that no torque works on H_2 in the dissociation. With this condition, K is always perpendicular to N and the rotation of H_2 originates only from that of the parent molecule. Conservation of energy and that of angular momentum are the same as those in case 3 ((A15) and (A16)). The rate of formation, $P(N)$, is expressed as

$$P(N) \propto \sum_v \sum_{(J,K)} \sum_{(I,K)} g(J) g'(K) \rho(E_k) \quad (A21)$$

where

$$D: |(J,I,K)| + K + N = J, K \perp N, \hbar|I| \leq (2m_H E_k)^{1/2} b_{\max} \quad (A22)$$

The definition of E_k is identical with that in (A17), and the

rotational distribution of H_2 , $g'(K)$, is assumed to be the Boltzmann distribution at 300 K. The condition that $K \perp N$ is treated in the counting of quantum states as follows: If $N \perp K$, i.e., $N \cdot K = 0$, the vector sum, M , of N and K is given by

$$|M|^2 = |N|^2 + |K|^2 \quad (A23)$$

The representation in which $|M|^2$, $|N|^2$, and $|K|^2$ are simultaneously diagonal being taken, one obtains that

$$M(M+1) = N(N+1) + K(K+1) \quad (A24)$$

Since M , N , and K are all integers, (A24) is not satisfied except by chance. Namely, the geometrical condition that $N \perp K$ is meaningful only in the classical limit, because the direction of the angular momentum is not observable in quantum mechanics. In the present analysis, M is calculated by solving (A24) with given N and K and then this value is replaced by the nearest integer.

Registry No. NH, 13774-92-0; NH₃, 7664-41-7; He, 7440-59-7.

Estimation of the Rate Constant of the $Ag^+ + Br^- \rightarrow AgBr$ Reaction. The Possibility of Non-Bromide-Controlled Oscillations in the Belousov-Zhabotinsky Reaction

Zoltan Noszticzius*[†] and William D. McCormick

Center for Nonlinear Dynamics and the Department of Physics, University of Texas, Austin, Texas 78712-9990 (Received: February 9, 1987; In Final Form: August 10, 1987)

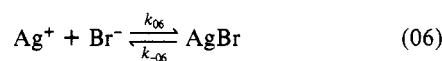
It has recently been proposed^{1,2} that the so-called non-bromide-controlled oscillations which have been observed to occur in the Belousov-Zhabotinsky reaction system in the presence of Ag^+ ions are, in fact, bromide controlled and that the experimental observations can be explained by a relatively slow $Ag^+ + Br^- \rightarrow AgBr$ reaction with $k \approx 10^4 \text{ M}^{-1} \text{ s}^{-1}$. In this paper experimental facts and theoretical arguments are presented that prove that the above-mentioned reaction is much faster. The problem of the response of a bromide-selective electrode during non-bromide-controlled oscillations is also discussed. The conclusion is that the original interpretation was correct and non-bromide-controlled oscillations do exist.

The most investigated oscillating chemical system is the Belousov-Zhabotinsky (BZ) reaction,³ the oxidation of an organic substrate by acidic bromate in the presence of a metal ion catalyst. It had always been assumed that, independent of the particular substrate or catalyst used, the role of the bromide ion in controlling the oscillations through a negative feedback loop was universal. However, a 1979 experiment by Noszticzius⁴ in which he found oscillations in a classical BZ system in the presence of silver ions caused some problems of interpretation. As Field³ points out, these non-bromide-controlled oscillations are the most difficult ones to rationalize within the framework of the FKN mechanism. In his experiment Noszticzius observed oscillations of the platinum electrode potential, but a simultaneous measurement with a bromide-selective electrode indicated a very low level of bromide ions which was changing monotonically.

In two recent papers Ruoff and Schwitters^{1,2} present calculations which seem to show that Noszticzius was wrong in the interpretation of his experimental results. In their first paper they use an Oregonator⁵ model to demonstrate that under certain assumptions bromide-controlled oscillations are still possible, even in the presence of silver ions. In their second paper they develop a theory explaining why the bromide electrode fails to indicate the calculated oscillations in the bromide level. At the end they conclude that the concept of non bromide ion control as first introduced by Noszticzius and then adopted by other authors^{3,6} is incorrect.

Ruoff and Schwitters' main argument is based on their hypothesis that the reaction between silver and bromide ions is

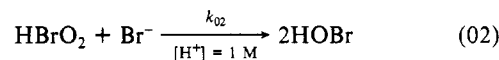
relatively slow. The model used in their calculations is the original Oregonator of Field and Noyes⁵ extended by a reversible precipitation reaction



where they assume, following an earlier suggestion by Ruoff,⁷ that

$$k_{06} = 10^4 \text{ M}^{-1} \text{ s}^{-1}$$

This value is relatively low compared to the rate constant of their reaction



which was assumed to be

$$k_{02} = 2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$$

The reaction 02 between the autocatalytic intermediate ($HBrO_2$) and the control intermediate (Br^-) is a crucial step in the Oregonator model. As long as inequality 1 is satisfied, silver ion cannot

$$k_{06}[Ag^+] \ll k_{02}[HBrO_2] \quad (1)$$

(1) Ruoff, P.; Schwitters, B. *J. Phys. Chem.* **1984**, *88*, 6424.

(2) Schwitters, B.; Ruoff, P. *J. Phys. Chem.* **1986**, *90*, 2497.

(3) Field, R. J. In *Oscillations and Traveling Waves in Chemical Systems*; Field, R. J.; Burger, M., Eds.; Wiley: New York, 1985; Chapter 2, p 55.

(4) Noszticzius, Z. *J. Am. Chem. Soc.* **1979**, *101*, 3660.

(5) Field, R. J.; Noyes, R. M. *J. Chem. Phys.* **1974**, *60*, 1877.

(6) Ganapathisubramanian, N.; Noyes, R. M. *J. Phys. Chem.* **1982**, *86*, 5155.

(7) Ruoff, P. *Chem. Phys. Lett.* **1982**, *92*, 239.

* Permanent address: Institute of Physics, Technical University of Budapest, H-1521 Budapest, Hungary.

compete with HBrO_2 for the bromide ion when the bromous acid concentration is high and the reaction network⁸ will not be seriously disturbed. In this case the bromide-controlled oscillations would be able to continue even in the presence of silver ions.

In this paper we should like to point out that experimental facts do not support Ruoff and Schwitters' hypothesis:

(i) Experimental evidence indicates that k_{02} is about 3 orders of magnitude smaller than was assumed by Ruoff and Schwitters. Noszticzius et al.⁹ estimated $k_{02} \approx 10^6 \text{ M}^{-1} \text{ s}^{-1}$ from their experiments. More accurate measurements reported by Ariese and Ungvárai^{10,11} confirmed this value. Calculations made by Tyson¹² and most recently by Field and Försterling¹³ and Noyes¹⁴ also support the lower value. We think it is not obvious that model calculations with a much lower k_{02} value will yield the same result even if k_{06} is as low as $10^4 \text{ M}^{-1} \text{ s}^{-1}$.

(ii) We have now done experiments to estimate k_{06} , however, and found that it is at least 2 orders of magnitude higher than was assumed by Ruoff and Schwitters. We injected Br^- ions into a 1 M H_2SO_4 solution containing Ag^+ ions while we measured the silver ion concentration using a silver electrode (silver wire of 1 mm diameter and of 5 mm length). The electrode potential is given by the Nernst equation:

$$E = E^\circ + 25.6 \text{ mV} \ln [\text{Ag}^+] \quad (2)$$

When the silver concentration is changing, the time derivative of the electrode potential is given by

$$\frac{dE}{dt} = 25.6 \text{ mV} \frac{1}{[\text{Ag}^+]} \frac{d[\text{Ag}^+]}{dt} \quad (3)$$

The rate equation according to (06) is

$$\frac{d[\text{Ag}^+]}{dt} = -k_{06}[\text{Ag}^+][\text{Br}^-] \quad (4)$$

Equation 4 assumes that the rate-limiting step is the slow reaction between silver and bromide ions. If the rate-determining step is the mixing or the response of the measuring system, then the measured rate of the whole process will be smaller than (4). Thus a calculation based on (4) will give a lower limit for k_{06} . Comparing (3) and (4) yields

$$\frac{dE}{dt} = -25.6 \text{ mV} k_{06}[\text{Br}^-] \quad (5)$$

In our experiments the initial conditions were the following: $[\text{Ag}^+]_0 = 10^{-5} \text{ M}$ and (after the injection of bromide, assuming an idealized well-mixed initial state without any reaction) $[\text{Br}^-]_0 = 2 \times 10^{-5} \text{ M}$. The result of the experiment can be seen in Figure 1. The slope of the electrode potential vs time diagram dE/dt was about -600 mV/s measured in the vicinity of the point where the silver ion concentration dropped to one-tenth of its initial value ($[\text{Ag}^+] = 10^{-6} \text{ M}$). The bromide concentration at this point was $[\text{Br}^-] = 1.1 \times 10^{-5}$ (calculated from the balance of reaction 06). Using these data

$$k_{06} \approx 2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$$

Our experiments showed clearly, however, that the rate-limiting step is the mixing of silver and bromide ions. (The slope of the electrode potential vs time curve was increasing with the increased rate of stirring.) Consequently, the real value of k_{06} must be even higher. Most probably the reaction between the negatively charged bromide ions and the positively charged silver ions is a diffusion-controlled reaction¹⁵ with a rate constant between 10^9 and $10^{10} \text{ M}^{-1} \text{ s}^{-1}$.

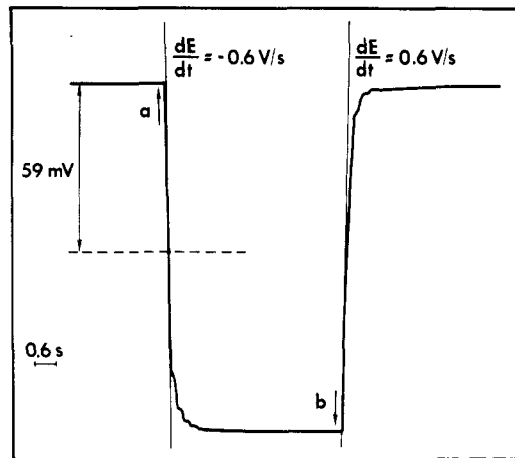


Figure 1. Potentiometric trace of a silver electrode during the $\text{Ag}^+ + \text{Br}^- \rightarrow \text{AgBr}$ reaction. At moment "a", denoted by an arrow in the figure, 0.1 cm^3 of 10^{-2} M NaBr solution was injected into a vigorously stirred solution of 50 cm^3 of 10^{-5} M AgNO_3 in 1 M H_2SO_4 . The solution was in a 100-cm^3 beaker, and the magnetic stirring was strong enough to generate a deep vortex. At moment "b" 0.1 cm^3 of 10^{-2} M AgNO_3 was injected into the same solution. The reference electrode was calomel connected via a "salt bridge" filled with 1 M H_2SO_4 . The temperature was $25 \pm 1^\circ \text{C}$.

The theoretical basis for assuming a diffusion-controlled reaction is the following. The rate-determining step in the ligand-substitution reactions is the removal of a water molecule from the inner coordination sphere and its replacement by a particle in the outer coordination sphere.^{16,17} It has been shown that the rate of this step is almost independent of the nature of the substituting ligand and depends primarily on the metal ion. According to Figure 3.5 in ref 16 all monovalent metal ions have characteristic substitution rates above 10^8 s^{-1} . The rate of substitution depends on the charge and the ionic radius.¹⁸ The ionic radius of Ag^+ is 1.13 \AA , which is between the ionic radius of Na^+ (0.95 \AA) and K^+ (1.33 \AA). (Data are taken from Table 2.10 of ref 16.) Both Na^+ and K^+ have a characteristic rate constant around 10^9 s^{-1} . Thus we can expect that Ag^+ should have a similar characteristic rate. To measure that rate, an adequate relaxation technique¹⁹⁻²¹ would be appropriate.

In addition to these conflicts with the experimental facts, we find that the theory of Ruoff and Schwitters explaining the response of a bromide-selective electrode in the BZ reaction in the presence of excess silver ions is difficult to accept. In particular, their treatment of the solubility equilibrium is unprecedented in the literature on ion-selective electrodes.²²⁻²⁴ They assume that in the bulk of the solution the solubility product is not satisfied, but directly at the interface of the electrode the solubility equilibrium holds. In other words, in the bulk of the solution the silver bromide precipitation reaction has to be slow but at the surface of the electrode it must be fast. Their argument for this difference is that otherwise the electrode potential would not be well-defined. The meaning of well-defined potential is not quite clear here. Most probably they mean the equilibrium potential. In that case the potential of the bromide-selective electrode can be easily calculated

(16) Basolo, F.; Pearson, R. G. *Mechanism of Inorganic Reactions*; Wiley: New York, 1967.

(17) Eigen, M. *Ber. Bunsen-Ges. Phys. Chem.* **1963**, *67*, 753.

(18) Diebler, H.; Eigen, M.; Ilgenfritz, G.; Maas, G.; Winkler, R. *Pure Appl. Chem.* **1969**, *20*, 93.

(19) Petrucci, S. In *Ionic Interactions*; Petrucci, S., Ed.; Academic: New York, 1971; Vol. 2, pp 39-124.

(20) Wilkins, R. G. *The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes*; Allyn and Bacon: Boston, 1974.

(21) Schelly, Z. A.; Eyring, E. M. *J. Chem. Educ.* **1971**, *48*, A639.

(22) Buck, R. P. In *Ion-Selective Electrodes in Analytical Chemistry*; Freiser, H., Ed.; Plenum: New York, 1978; Vol. 1, pp 1-142.

(23) Pungor, E.; Toth, K. In *Ion-Selective Electrodes in Analytical Chemistry*; Freiser, H., Ed.; Plenum: New York, 1978; Vol. 1, pp 143-210.

(24) Pungor, E., Ed.; *Ion-Selective Electrodes 4. Fourth Symposium*, Elsevier: Amsterdam, New York, 1985.

(8) Clarke, B. *Adv. Chem. Phys.* **1980**, *43*, 1.

(9) Noszticzius, Z.; Noszticzius, E.; Schelly, Z. A. *J. Phys. Chem.* **1983**, *87*, 510.

(10) Ariese, F.; Ungvárai-Nagy, Zs. *J. Phys. Chem.* **1986**, *90*, 1.

(11) Ariese, F.; Ungvárai-Nagy, Zs. *J. Phys. Chem.* **1986**, *90*, 1496.

(12) Tyson, J. J. In *Oscillations and Traveling Waves in Chemical Systems*; Field, R. J.; Burger, M., Eds.; Wiley: New York, 1985; Chapter 3, p 93.

(13) Field, R. J.; Försterling, H. D. *J. Phys. Chem.* **1986**, *90*, 5400.

(14) Noyes, R. M. *J. Phys. Chem.* **1986**, *90*, 5407.

(15) Noyes, R. M. *Prog. React. Kinet.* **1961**, *1*, 129.

either from the silver or from the bromide concentration exclusively and we get the same result. (They emphasize that the solubility product must be fulfilled in order to get a single well-defined potential.) Nevertheless, nonequilibrium electrode potentials might be difficult to calculate but they can be quite stable. The mere fact that we measure an electrode potential is not a proof for an equilibrium situation. In this case, however, the solubility equilibrium is satisfied both at the surface of the electrode and in the bulk of the solution as usual. This is not because of the necessity for a well-defined electrode potential but because the reaction between silver and bromide ions is very fast.

Thus we can conclude that the interpretation of the original experiments on BZ oscillations in the presence of Ag^+ ions was correct and that due to the $\text{Ag}^+ + \text{Br}^- \rightarrow \text{AgBr}$ reaction the bromide ion concentration is too low to play the role of a control intermediate in these systems.

Acknowledgment. We thank Prof. Harry L. Swinney for helpful discussions and Maria Gerencser for the experiments. This work was partially supported by the Robert A. Welch Foundation and by the Texas Advanced Technology Research Program.

Registry No. Ag^+ , 14701-21-4; Br^- , 24959-67-9.

Thermalization of Energetic ^{18}F Atoms for Gas-Phase Reaction with Propene

Patricia J. Rogers and F. S. Rowland*

Department of Chemistry, University of California, Irvine, California 92717 (Received: March 25, 1987;
In Final Form: July 8, 1987)

The gas-phase reactions of radioactive ^{18}F atoms with propene have been studied over the pressure range from 500 to 4000 Torr in mixtures with $[\text{SF}_6]/[\text{C}_3\text{H}_6]$ mole ratios varying from 100 to 1000. The SF_6 molecules serve both as the ^{19}F target for the $^{19}\text{F}(\text{n},2\text{n})^{18}\text{F}$ fast neutron reaction and as the moderator for removing the excess kinetic energy imparted to the ^{18}F atoms by nuclear recoil. Moderator/substrate ratios >100 are large enough that hot atom reactions have been suppressed to yields well below 1%, with almost all ^{18}F atoms reacting as thermal atoms. Three thermal reactions are dominant with propene, with yields of about 32% for terminal addition to form $\text{CH}_3\text{CHCH}_2^{18}\text{F}^*$; 23% for central addition to form $\text{CH}_3\text{CH}^{18}\text{FCH}_2^*$; and 45% for abstraction of H to form H^{18}F . Terminal addition is favored over central addition for thermal ^{18}F atoms by a factor of 1.35 ± 0.05 . The competitive thermal reactions of ^{18}F have also been studied with mixtures of propene and HI in these highly moderated systems. Stabilized $\text{C}_3\text{H}_6^{18}\text{F}$ radicals are assayed as $\text{C}_3\text{H}_7^{18}\text{F}$ after scavenging by reaction with HI, and the relative total reactivity of propene versus HI can be evaluated from the diminution in the yields of these products with increasing $[\text{HI}]/[\text{C}_3\text{H}_6]$ mole ratio. The relative reactivity of HI versus $\text{CH}_3\text{CH}=\text{CH}_2$ toward thermal fluorine atoms is 0.36 ± 0.03 , indicating an absolute reaction rate for fluorine atoms with propene of $(1.8 \pm 0.3) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Collisions of atomic fluorine with the olefinic electron cloud react by addition with a probability approaching unity. A complementary pressure dependence is observed between stabilized (and scavenged) $\text{CH}_3\text{CH}^{18}\text{FCH}_2^*$ and its decomposition product $\text{CH}_2=\text{CH}^{18}\text{F}$; negligible yields of any but the stabilization product are found at 500 Torr SF_6 for $\text{CH}_3\text{CHCH}_2^{18}\text{F}^*$ radicals. Decomposition of $\text{CH}_3\text{CH}^{18}\text{FCH}_2^*$ radicals is approximately equal to collisional stabilization at an (extrapolated) pressure of 55 ± 10 Torr. The decomposition rate constant is about $(2-4) \times 10^8 \text{ s}^{-1}$ and is consistent with reaction rates calculated by RRKM theory for the decay of $\text{CH}_3\text{CH}^{18}\text{FCH}_2^*$ radicals. The yields of $\text{CH}_2=\text{CH}^{18}\text{F}$ have been extrapolated to infinite pressure and demonstrate nonzero intercepts corresponding to yields of 0.1-0.2%. Our data are not precise enough to assign these nonzero intercepts among possible mechanisms involving (a) the addition of still energetic ^{18}F atoms to the central olefinic position; (b) direct substitution of F for CH_3 initiated by hot ^{18}F atoms; or (c) such direct substitution initiated by thermal ^{18}F atoms.

Introduction

Radioactive ^{18}F atoms from the $^{19}\text{F}(\text{n},2\text{n})^{18}\text{F}$ nuclear reaction have many advantages for the study of thermal fluorine atom reactions. However, these atoms are created with kinetic recoil energies of $>10^5 \text{ eV}$ and consequently have the opportunity first to react "hot" while still possessing excess kinetic energy.¹⁻⁹ The reactivities of gaseous substrate molecules toward recoil ^{18}F atoms vary widely, with some such as SF_6 ¹⁻⁶ and CF_4 ⁷⁻⁹ almost inert despite the extra kinetic energy available. Our earlier studies of gaseous mixtures with SF_6 characterized most of the observed reactions as "near thermal" when ^{18}F reacted with the minor components in the system at mole fractions less than 0.1.^{2,4} The

utility of such "thermalized" ^{18}F atoms for true thermal studies is then dependent upon detailed knowledge of the extent of possible nonthermal reactions in such systems. Our gas-phase experiments reported here have explored the mixture of hot and thermal reactions found for ^{18}F with propene in the presence of large excesses of SF_6 . We have reduced the mole fraction of propene in SF_6 from the 0.05-0.10 of the near-thermal experiments down into the range from 0.01 to 0.001. Hydrogen iodide has often been included in the irradiated gas mixture in low mole fraction to scavenge chemically ^{18}F -labeled radicals stabilized by collisions.

If the mole fraction of reactive competitors such as propene and hydrogen iodide is low enough, then the average number of collisions required for nonreacting atomic fluorine through the 20 eV-to-thermal range is determined essentially entirely by energy loss in encounters with SF_6 , and is independent of the moderating collision characteristics of the minor components. Under these conditions, the collision probability for energetic ^{18}F atoms with propene is proportional to its mole fraction multiplied by the collision cross section ratio for $[\text{C}_3\text{H}_6]/[\text{SF}_6]$. Successful ^{18}F -bond formation in hot reaction will then also be proportional to the mole fraction of reactive substrate. Failure of these approximations is expected when (a) the overall probability of hot reaction is sufficiently high that appreciable fractions of the hot atoms are removed by such energetic reactions ("shadowing"), or (b) the

- (1) Rowland, F. S.; Rust, F.; Frank, J. P. *ACS Symp. Ser.* **1978**, *66*, 26.
- (2) Smail, T.; Iyer, R. S.; Rowland, F. S. *J. Phys. Chem.* **1972**, *95*, 1041.
- (3) Williams, R. L.; Iyer, R. S.; Rowland, F. S. *J. Am. Chem. Soc.* **1972**, *94*, 7192.
- (4) Williams, R. L.; Rowland, F. S. *J. Phys. Chem.* **1971**, *75*, 2709.
- (5) Williams, R. L.; Rowland, F. S. *J. Phys. Chem.* **1973**, *77*, 301.
- (6) Williams, R. L.; Rowland, F. S. *J. Phys. Chem.* **1972**, *76*, 3509.
- (7) Mathis, C. A.; Knierim, K. D.; Root, J. W. *Chem. Phys. Lett.* **1980**, *72*, 368.
- (8) Root, J. W. *Adv. Chem. Ser.* **1981**, *197*, 228.
- (9) Mo, S.-H.; Grant, E. R.; Little, F. E.; Manning, R. G.; Mathis, C. A.; Werre, G. S.; Root, J. W. *ACS Symp. Ser.* **1978**, *66*, 59.