of this substrate.[6] We have now searched for them again and observed only faint traces of their absorption in the visible region after the initial deposition or irradiation at 11 K. It appears very likely that Fe(CO)$_5$, and its photodecomposition products, are efficient scavengers of both H and F centers. It is then understandable that their presence will suppress the H-center-catalyzed phototransformation **2** → **1**.

In summary, we believe that we have demonstrated the catalysis of an organic isomerization reaction by solid alkali halides, specifically, by color centers present in these solids. This has obvious implications for the use of alkali halides as "inert" matrices,[1,6] but may also be of more general interest, since catalysis by solid alkali halides is rather unusual. For instance, they were not even mentioned in a recent survey of catalysis by non-metals.[49] Some alkali halides are used as promoters in industrial heterogeneous catalysis, the mechanism of their action being quite obscure.[50] A photocatalytic effect of KBr and CsI has been reported for the photodecomposition of vinyl chloride[51] but the mechanism has not been investigated.

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Registry No. 1, 121-46-0; **2**, 278-06-8.

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(49) *Surface Properties and Catalysis by Non-Metals*; Bonnelle, J. P., Delmon, B., Derouane, E., Eds.; NATO ASI Series, D; Reidel Publishing Co.: Dordrecht, Holland, 1983.

(50) Kiso, Y.; Saeki, K.; *J. Organomet. Chem.* **1986**, *303*, C-17.

(51) Woldback, T.; Klaboe, P. *Spectrochim. Acta A* **1978**, *34A*, 481.

Propagating Reaction Front in the Cobalt(II)-Catalyzed Autoxidation of Benzaldehyde

E. Boga, G. Peintler, and I. Nagypál*

Contribution from the Department of General and Physical Chemistry, Attila József University, H-6701 Szeged, P.O. Box 105, Hungary. Received June 19, 1989

Abstract: A propagating reaction front was found and investigated in the dissolved oxygen–Co(Ac)$_2$–benzaldehyde closed system in glacial acetic acid. The velocity of the front increases with the concentrations of benzaldehyde and dissolved oxygen and decreases with [Co(Ac)$_2$]. The experimental findings are interpreted on the basis of a simplified version of a proposed mechanism of the reaction. This is the first chemical wave reported in a nonaqueous solvent.

The liquid-phase oxidation of organic compounds by molecular oxygen catalyzed by transition metal ions has been a subject of detailed studies[1,2] for many years. Most of these reactions are autocatalytic and characterized by radical chain mechanisms. These features may result in exotic kinetic behavior, such as bistability, oscillation, and propagating reaction fronts. Oscillation has been observed and interpreted in the Co(II)-catalyzed oxidation of benzaldehyde in aqueous acetic acid in the presence of Br$^-$ ion[3,4] in an open system where the reaction mixture may take up oxygen.

The autocatalytic nature of the reaction raises the possibility of propagating reaction fronts.[5,6] Our preliminary experiments demonstrated that a propagating front could be initiated in the system by perbenzoic acid or by Co(III), which are known[7-9] intermediates of the overall reaction. The results of systematic studies of the concentration dependence of the velocity of the propagating front are reported and interpreted in the present paper.

Experimental Section

Benzaldehyde of analytical purity was distilled three times under vacuum in a nitrogen atmosphere from anhydrous K$_2$CO$_3$ and kept protected from light under nitrogen. Analytically pure, "chromic acid resistant" 99% acetic acid was freed from water with acetic anhydride. Its water content was less than 0.001%.

Co(Ac)$_2$·4H$_2$O (BDH) was purified by double recrystallization from aqueous acetic acid. It was dried to constant weight at 100 °C and 1.5 Torr, then stored over P$_2$O$_5$. Perbenzoic acid was prepared from dibenzoyl peroxide by the method of Braun.[10]

Oxygen-nitrogen mixtures (see later) were purged through an acetic acid solution of cobalt(II) acetate for 30 min through a filter containing P$_2$O$_5$ and pumice. This interval was found to be suitable for saturation of the solution. Then benzaldehyde was added, and after complete mixing the solution was pulled into a capillary tube of 1-mm internal diameter. The wave was initiated by immersing the end of the tube for a moment in a solution of 0.05 M perbenzoic acid in acetic acid. The perbenzoic acid caused the pink color of Co(II) to change to green Co(III), and this front started to travel along the tube. The propagating front was followed visually in the horizontal direction. The measurements were carried out at ambient room temperature of 22 ± 2 °C.

Results and Discussion

Figure 1 shows the distance versus time curves at four different Co(II) concentrations. The velocity of the front as a function of the concentration of the individual components is illustrated in Figures 2–4.

A quantitative characterization of the concentration dependence of the front velocity has been given only in very few cases.[5] Because of the complexity of the present system, no quantitative

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(1) Reich, L.; Stivala, S. S. *Autoxidation of Hydrocarbons and Polyolefins*; Marcel Dekker: New York, 1969.

(2) Scott, G. *Atmospheric Oxidation and Antioxidants*; Elsevier: Amsterdam – New York, 1965.

(3) Roelofs, M. G.; Wasserman, E.; Jensen, J. H. *J. Am. Chem. Soc.* **1987**, *109*, 4207–4217.

(4) Yuan, Z.; Noyes, R. M. In *Spatial Inhomogenities and Transient Behaviour in Chemical Kinetics*; Brussels, 1987; Abstract of Papers p 72.

(5) Showalter, K. In *Kinetics of Nonhomogeneous Processes*; Freeman, G. R., Ed.; Wiley: New York, 1987, pp 769–821.

(6) Szirovicza, L.; Nagypál, I.; Boga, E. *J. Am. Chem. Soc.* **1989**, *111*, 2842–2845.

(7) Bawn, C. H. E.; Jolley, J. E. *Proc. R. Soc., London, Ser. A* **1956**, *237*, 297–312.

(8) Márta, F.; Boga, E.; Matók, M. *Discuss. Faraday Soc.* **1968**, *46*, 173–183.

(9) Chalk, A. J.; Smith, J. F. *Trans. Faraday Soc.* **1957**, *53*, 1214.

(10) Braun, G. *Org. Synth.* **1948**, *1*, 431.

0002-7863/90/1512-151$02.50/0

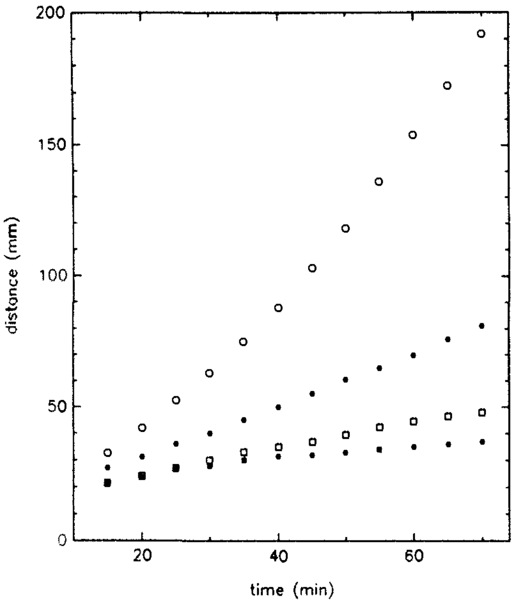

Figure 1. Position of the front as a function of time at different $Co(Ac)_2$ concentrations: [PhCHO] = 0.754 M; $[O_2]$ = 0.0083 M (saturated); $[Co(Ac)_2]$ = 0.005 M (○), 0.012 M (●); 0.016 M (□); 0.024 M (■).

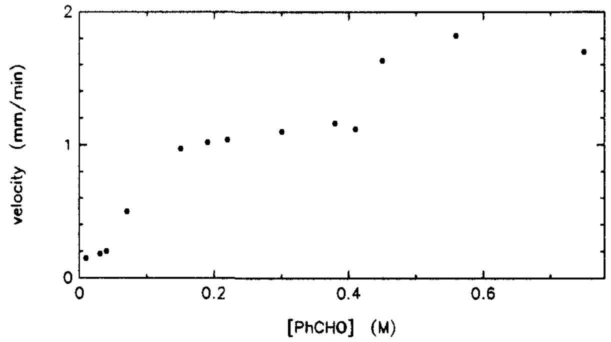

Figure 2. The effect of benzaldehyde concentration on the velocity of the front: $[Co(Ac)_2]$ = 0.007 M, $[O_2]$ = 0.0083 M (saturated).

description of the concentration dependence of the wave velocity is attempted. The mechanism of the reaction is extremely complicated; the simulation of the oscillatory behavior in an open system in presence of Br^- ions involves 21 elementary steps.[3] For a qualitative interpretation of our present results, we propose the following "skeleton" mechanism, including rate constants where available. (The fine details of the mechanism, such as the dimerization of Co(II) and Co(III) acetate, etc., are deliberately omitted.)

$$\mathrm{PhCOOOH + Co(II) \rightarrow PhCOO^{\bullet} + Co(III) + OH^-} \qquad (R_1)^{15}$$

$$v_1 = 1.9 \times 10^5[\mathrm{PhCOOOH}][\mathrm{Co(II)}]$$

$$\mathrm{Co(III) + PhCHO \rightarrow Co(II) + PhCO^{\bullet} + H^+} \qquad (R_2)^{8,16,17}$$

$$v_2 = 1.6 \times 10^{-4}[\mathrm{Co(III)}][\mathrm{PhCHO}]^2$$

$$\mathrm{PhCO^{\bullet} + O_2 \rightarrow PhCOOO^{\bullet}} \qquad (R_3)^3$$

$$v_3 = 5.0 \times 10^8[\mathrm{PhCO^{\bullet}}][\mathrm{O_2}]$$

$$\mathrm{PhCOOO^{\bullet} + PhCHO \rightarrow PhCO^{\bullet} + PhCOOOH} \qquad (R_4)^{3,16}$$

$$v_4 = 3.9 \times 10^3[\mathrm{PhCOOO^{\bullet}}][\mathrm{PhCHO}]$$

$$\mathrm{PhCOOO^{\bullet} + Co(II) \rightarrow Co(III) + PhCOOO^-} \qquad (R_5)^{11}$$

$$v_5 = 8 \times 10^6[\mathrm{PhCOOO^{\bullet}}][\mathrm{Co(II)}]$$

$$\mathrm{PhCOO^{\bullet} + PhCHO \rightarrow PhCO^{\bullet} + PhCOOH} \qquad (R_6)^3$$

$$v_6 = 1 \times 10^7[\mathrm{PhCOO^{\bullet}}][\mathrm{PhCHO}]$$

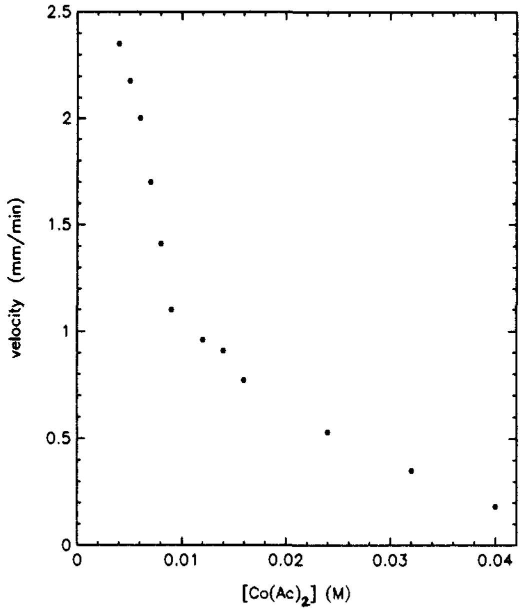

Figure 3. The effect of Co(II) acetate concentration on the velocity of the front: [PhCHO] = 0.754 M, $[O_2]$ = 0.0083 M (saturated).

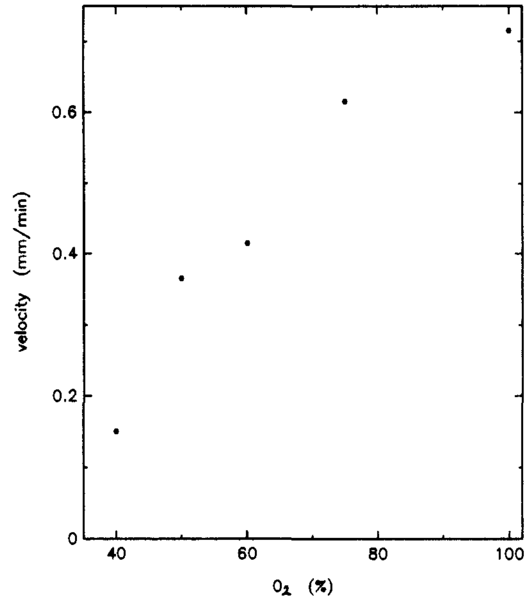

Figure 4. The effect of the oxygen content of the O_2–N_2 mixture used to saturate the solutions studied on the velocity of the front propagation.

The appropriate combination of the individual steps shows that the accumulation of perbenzoic acid is autocatalytic.

$$R_1 + R_2 + 2R_3 + 2R_5 + R_6 \qquad (R_7)$$

$$\mathrm{PhCOOOH + 2PhCHO + 2O_2 + 2Co(II) = 2PhCOOOH + 2Co(III) + PhCOO^- + OH^-} \qquad (R_8)$$

From an analysis of the skeleton mechanism and the above equations, taking into account the results of some additional experiments, the following can be stated.

a. According to (R_2), the reaction front can be initiated by Co(III). Additional experiments confirm this expectation.

b. If we completely eliminate perbenzoic acid, then there would be no pathway for spontaneous initiation of the reaction. The practically unavoidable perbenzoic acid content of the benzaldehyde may explain the observation that the reaction mixture is not stable at high benzaldehyde concentration. At [PhCHO] > 1 M, the bulk reaction becomes too fast under our experimental conditions; thus the Co(II)–Co(III) transition is complete within minutes.

c. The Co(II) acts as a catalyst at low concentration but inhibits the reaction at high concentration. The catalytic effect is clearly seen from (R_1) and (R_2). At high Co(II), however, the radicals produced can not build up sufficiently to initiate the propagation of the reaction through (R_3) and (R_4), because they are quickly consumed by (R_5). This is in agreement with the velocity-decreasing effect of [Co(II)] and with earlier results.[11-14] In accordance with the opposing effects, we have found that the "bulk" reaction taking place in the capillary tube without initiation is too fast for waves to be measured at $[Co(Ac)_2] < 0.004$ M; i.e., the reaction is complete soon after mixing the components. Therefore, we could not carry out experiments at sufficiently low Co(II) concentration to illustrate the catalytic effect. At the same time, no wave could be initiated at all at $[Co(Ac)_2] > 0.04$ M under our experimental condition, because the inhibitory effect prevents the wave propagation. At low Co(II) concentration the wave accelerates because of the bulk reaction, as seen in Figure 1. (The diffusion of the perbenzoic acid used to initiate the reaction may influence the velocity within the first 10–15 mm; thus the initial parts of the curves are not shown.)

d. According to the skeleton mechanism, an increase in [Co(II)] increases the rate of the bulk reaction. This is in agreement with our observation that at high Co(II) concentration ($[Co(Ac)_2] >$ 0.02) the pink color of the solution before the front slowly changes to applegreen, causing the disappearence of the sharp boundary within 1-2 h. (This does not necessarily mean that the perbenzoic acid front comes to an end, only that the front cannot be observed visually any further.)

e. At intermediate Co(II) concentration a "second" front following the first one can be observed, where the green Co(III) color changes back to pink Co(II). This phenomenon also limits the observable time interval to about 1–2 h.

f. The velocity of the front propagation as a function of the percentage oxygen content of the O_2–N_2 mixture used to saturate the solution is seen in Figure 4. No visual observation of the front was possible with $O_2 < 40\%$. Figure 4 suggests that there is a threshold in O_2 concentration below which no wave can be initiated. The reason is that below this limit the dissolved O_2 is completely consumed by Co(II), and no excess is available to produce perbenzoic acid, which is responsible for the propagation of the wave.

Conclusion

The present paper is the first report on the phenomenon of propagating reaction fronts in the autoxidation process and in a nonaqueous solution. Since most autoxidation processes of organic compounds follow a similar mechanism, the discovery of many other waves can be anticipated. The mechanistic details of these type of reactions are well known. Thus the extension of experimental studies in this field is a promising venture and may be of a great value in understanding nonlinear phenomena in chemical kinetics.

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Registry No. PhCHO, 100-52-7; $Co(Ac)_2 \cdot 4H_2O$, 6147-53-1; O_2, 7782-44-7.

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(11) Niki, E.; Kamiya, Y. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 1095.
(12) Betts, A. T.; Uri, N. *Macromol. Chem.* **1966**, *95*, 22.
(13) Denisov, E. T.; Emanuel, N. M. *Zh. Phys. Khim.* **1956**, *30*, 2499.
(14) Boga, E.; Márta, F. *Acta Chim. Acad. Sci. Hung.* **1973**, *78*, 193.
(15) Jones, G. H. *J. Chem. Soc., Chem. Commun.* **1979**, 536–537.
(16) Boga, E.; Kiricsi, I.; Deér, A.; Márta, F. *Acta Chim. Acad. Sci. Hung.* **1973**, *78*, 89.
(17) Sharp, J. A. *J. Chem. Soc.* **1957**, 1866.

Partial Molar Volumes of Sulfur Dioxide in Organic Solvents: Formation of Charge-Transfer Complexes

John F. Smith, Gerald A. Bottomley,[1] Leslie Barta, and Loren G. Hepler*

Contribution from the Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2. *Received March 14, 1989*

Abstract: New apparatus for measuring the apparent molar volumes of gases in liquids is described. The apparatus has been used to obtain the limiting partial molar volume of sulfur dioxide in 17 organic solvents. The limiting partial molar volume of sulfur dioxide is found to be significantly smaller in electron-donating solvents than in non-electron-donating solvents, with this difference being interpreted in terms of charge-transfer complex formation. We propose two methods for estimating the standard volume change of the complexation reaction and illustrate the use of these methods by application to the sulfur dioxide + benzene system.

Many investigators have shown that sulfur dioxide forms charge-transfer complexes with electron donors. Evidence has been reported for complex formation between sulfur dioxide and aromatic hydrocarbons, olefinic hydrocarbons, and hydrocarbons containing a heteroatom. Accounts of some representative studies can be found in ref 2–10.

Since the formation of charge-transfer complexes will lead to enhanced solubility of sulfur dioxide in electron-donating solvents, such solvents may have industrial importance as good absorbents for removing sulfur dioxide from gaseous effluents.[11] Further investigation of this possibility requires knowledge of the solubility of sulfur dioxide in electron-donating solvents.

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(1) Visiting Professor from the Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands, WA 6009, Australia.
(2) Locket, G. H. *J. Chem. Soc.* **1932**, 1501–1512.
(3) Andrews, L. J.; Keefer, R. M. *J. Am. Chem. Soc.* **1951**, *73*, 4169–4172.
(4) de Maine, P. A. D. *J. Chem. Phys.* **1957**, *26*, 1036–1056.
(5) Booth, D.; Dainton, F. S.; Ivin, K. J. *Trans. Faraday Soc.* **1959**, *55*, 1293–1309.
(6) Smith, B. C.; Smith, G. H. *J. Chem. Soc.* **1965**, 5514–5516.
(7) Santos, P. S.; Isolani, P. C. *Chem. Phys. Lett.* **1979**, *67*, 487–490.
(8) Tse, J. S.; Ripmeester, J. A. *J. Phys. Chem.* **1983**, *87*, 1708–1712.
(9) Adams, W. A.; Kruus, P.; Patraboy, T. J. *Can. J. Chem.* **1983**, *61*, 37–44.
(10) Gardner, C. L.; Day, R. W. *Can. J. Chem.* **1984**, *62*, 986–989.
(11) Benoit, R. L.; Milanova, E. *Can. J. Chem.* **1979**, *57*, 1319–1323.