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DISCLAIMER

RESPONSE TO COMMENTS ON "KINETICS OF ENDOTHERMIC DECOMPOSITION REACTIONS. 2. EFFECTS OF SOLID AND GASEOUS PRODUCTS."

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Response to Comments on "Kinetics of Endothermic Decomposition Reactions. 2. Effects of Solid and Gaseous Products."

Dear Sir:

As Dr. Bertrand points out (see Comment above), under many experimental conditions decomposition rates are limited by rates of heat transfer or gas phase diffusion. Furthermore, different portions of large samples are usually subjected to different thermal fluxes and to different local product gas pressures and in consequence decompose at different rates. For these reasons, we share his pessimism about developing a theory that will predict decomposition rates for arbitrarily set conditions. However, our experimental and theoretical studies are directed not toward the prediction of rates under such complex circumstances, but toward developing a better understanding of the chemical mechanisms of decomposition reactions.

For this purpose, we have adopted[1] an experimental strategy that has proved highly successful in studies of the kinetics of congruent vaporization.[2] This strategy is to establish conditions under which neither heat transfer nor gas phase diffusion limits reaction rates. We work with low reaction fluxes, with near-black body radiation heating, and with small samples of known surface areas. Then phemonena such as the Smith-Topley effect,[3] which Dr. Bertrand and his colleagues have shown to be consequences of thermal gradients,[4] do not obscure the chemical kinetics.

Although our experimental strategy simplifies the problem of theoretical interpretation of decomposition reaction data, that problem still remains more formidable than for congruent vaporization. Most

theoretical treatments of decomposition reactions have assumed without comment that only a single chemical process, usually a process on the reactant surface, need be considered.[5] But as a decomposition reaction, say AB(s) → A(s) + B(g), proceeds a usual consequence is that small volume elements that originally contained AB(s) are replaced by smaller volume elements of A(s) plus pores. In our theoretical papers[6,7] we argued that this observation implies that for such a decomposition reaction, not only the slowest surface reaction step, but also three additional condensed phase steps, as well as escape of the gaseous product through the porous solid product, must proceed concurrently and that, in principle, any of these five processes may be slow enough to influence the decomposition rate. We then derived limiting rate equations, which predicted the dependence of measured rates on product gas pressure, on possible metastability of the solid product, and on the pore dimensions of the solid product.

Dr. Bertrand questions whether our four condensed phase steps are sufficient to describe all endothermic decomposition reactions that yield porous products, and he also questions whether our designated four steps are all necessary.

We have always agreed that when experimental data justified doing so, one or more of the condensed phase steps could be further subdivided. For example, in interpreting data for $BaCO_3$ decomposition,[8] we subdivided the surface step of our model into a desorption step and an earlier surface step and concluded that the desorption could not be rate limiting, but that an earlier surface step could be. We hope that experimental data may sometimes be of sufficient quality to warrant the

use of still more complex models of the surface step[9,10] or of other reaction steps.[7]

We are persuaded by the evidence cited by Dr. Bertrand[11,12] that the movement of the solid reaction component A and its interfacial transfer step, which our model assumes to be separable, sometimes can occur in a single step, a strain-induced transformation. If so, the strain-induced transformation must form the solid reaction product A(s) at a rate coupled to the rate of diffusion of the gaseous reaction component B from inside the solid reactant phase AB to the surface and of a surface transfer step for B.

Cooperative phenomena such as strain-induced transitions presumably occur very rapidly throughout a small volume element of AB(s) whenever the stress level exceeds a critical value. For decomposition reactions, the stress presumably is a consequence of depletion of B in the reactant phase near the reaction front. Thus the rate limiting process must be condensed phase diffusion of B, and the rate law applicable for decomposition in vacuum should be that derived[6] on the assumption that the condensed phase diffusion step of B is the slowest step of decomposition.

We do not expect, however, that if the solid product is formed by a strain-induced transition, the rate will show the simple linear decrease with increased product gas pressure that is predicted by our model.[7] When the gas pressure has become high enough to maintain the concentration of B at a level too high to permit cooperative movement of volume elements of the size that transform in vacuum, a new steady state may be established in which the transition results from a lower level of unit strain which has accumulated in larger volume elements of

the reactant. We plan to investigate this interesting problem.

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REFERENCES

1. D. Beruto and A. W. Searcy, J. Chem. Soc., Far. Trans. 1, 70, 2145 (1974).
2. P. Hart and A. W. Searcy, J. Phys. Chem., 70, 2763 (1966).
3. B. Topley and M. L. Smith, J. Chem. Soc., 1935 321.
4. G. Bertrand, M. Lallemant, A. Mokhlisse, and G. Watelle - Marion J. Inorg. Nucl. Chem., 40, 819 (1978).
5. See for example the reviews given by D. A. Young, "Decomposition of Solids," Pergamon Press, Oxford, 1966 and K. H. Stern and E. L. Weise, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand., No. 30 (1969).
6. A. W. Searcy and D. Beruto, J. Phys. Chem., 80, 425 (1976).
7. A. W. Searcy and D. Beruto, ibid. 82, 163 (1978).
8. T. K. Basu and A. W. Searcy, J. Chem. Soc., Faraday Trans. 1, 72, 1889 (1976).
9. P. Barret, C. R. Acad. Sci., 266C, 856 (1968).
10. A. W. Searcy and D. Beruto, J. Phys. Chem., 78, 1298 (1974).
11. J. C. Niepce and G. Watelle, J. Mat. Sci., 13, 149 (1978).
12. C. L. Cronan, F. J. Micale, M. Topic, H. Leidheiser, A. C. Zettlemoyeur, and S. Popovic, J. Colloid. Interface Sci., 55, 546 (1976).

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