In these latter experiments there is a serious dilution effect on any selectivity shown by the primary particle, due to the extensive radiation chemical effects of secondary electrons (δ-rays) of very much lower polarization, which also interact with the racemic medium. In order to avoid this, some experiments were conducted with an equal mixture of enantiomeric crystals, rather than a racemate on the molecular level. When irradiated with polarized high-energy protons (500 MeV) the crystals gave results which indicated less than a 2% selectivity;[98] but these experiments will be repeated with 100% longitudinally polarized surface muons (4 MeV) when the intensity needed is available. With these muons the crystal size can be matched to the secondary electron's range so that, every time a primary (selective) interaction occurs, all the energy released by the interaction causes decomposition of only the one enantiomer involved in the primary step.

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ARTICLES

Effect of CO_2 Pressure on the Rate of Decomposition of Calcite

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Rates of CO_2 escape from $(10\bar{1}1)$ cleavage surfaces of calcite ($CaCO_3$) single crystals were measured at temperatures from 893 to 1073 K and at CO_2 background pressures, P_{CO_2}, from $<P_L = 10^{-5}P_{eq}$ to $4 \times 10^{-2}P_{eq}$, where P_{eq} is the equilibrium decomposition pressure and P_L is the CO_2 pressure that produces a flux equal to the flux from a calcite crystal under vacuum. Rates are relatively sensitive to P_{CO_2} when $P_{CO_2} > 10^{-2}P_{eq}$, but do not obey the parabolic rate law deduced by earlier investigators from data in a limited pressure range. For $P_L < P_{CO_2} < 10^{-2}P_{eq}$, the decomposition rates are essentially independent of P_{CO_2}, which implies that in this range the apparent activation enthalpy and entropy are unchanged from those measured under vacuum, $\Delta H^* = 209 \pm 12$ kJ (50 ± 3 kcal) and $\Delta S^* = 84 \pm 12$ J/deg (20 ± 3 cal/deg). The rate-limiting process in this pressure range is probably condensed-phase diffusion of CO_2 or a surface step for CO_2 prior to desorption.

Introduction

Endothermic decomposition reactions of the general form AB(s) = A(s) + B(g) have been poorly understood. For example, these reactions are commonly described as reversible, but carbonate and sulfate decomposition reactions studied in our laboratory[1–4] occur at only 10^{-3} to 10^{-5} times the maximum rates which can be calculated for them from the equilibrium decomposition pressure, P_{eq}, and the Hertz–Knudsen–Langmuir equation. Reactions that are thermodynamically reversible would occur at the maximum rate.

Searcy and Beruto have provided a model that predicts the influence of the experimental variables of temperature, pressure, and thermodynamic stability of the reaction product, and pore geometry of the reaction product on the decomposition rates when any one of several steps of the overall decomposition process[5,6] is rate limiting. Application of the model is being tested with calcite ($CaCO_3$). The influence of extent of reaction,[1,4] temperature,[1,4] heat transfer,[4] and CaO pore geometry[7] on rates of decomposition of single crystals under vacuum have been reported.

The effect of CO_2 background pressure on calcite decomposition rates has already been studied by Hyatt, Cutler, and Wadsworth[8] and by Cremer and Nitsch.[9] Both sets of investigators concluded that the rate is proportional to $1/P_{CO_2}$, where P_{CO_2} is the CO_2 pressure. But Hyatt et al. varied CO_2 pressures by only about a factor of 10 at any fixed temperature. Cremer and Nitsch used a still more limited range of pressures and furthermore used powdered calcite samples, for which the effects of particle size and bed depth are not established. The meaningful range for study of CO_2 pressure dependence extends from the equilibrium decomposition pressure, P_{eq},

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(1) D. Beruto and A. W. Searcy, *J. Chem. Soc., Faraday Trans. 1*, **70**, 2145 (1974).

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(7) J. A. Roberts, N. S. Jacobson, and A. W. Searcy, *J. Chem. Phys.*, **69**, 5562 (1978).

(8) E. P. Hyatt, I. B. Cutler, and M. E. Wadsworth, *J. Am. Ceram. Soc.*, **41**, 70 (1958).

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down to $P_{CO_2} = P_L \simeq 10^{-5}P_{eq}$, for which the flux of CO_2 gas against the $CaCO_3$ crystal equals the flux that leaves the surface when the $CaCO_3$ is decomposed under vacuum. For, $P_{CO_2} > P_L$ decomposition cannot occur unless the probability of recombination is $<P_L/P_{CO_2}$.

In this paper we report the effect on the decomposition rate of CO_2 pressure from $<P_L$ to $\simeq 4 \times 10^{-2}P_{eq}$. The implications of the results are discussed in terms of the Searcy and Beruto model and of that model as modified if formation of the CaO phase occurs not by diffusion and an interface transfer step but by a cooperative process such as shear,[10] which cannot be described by chemical rate equations.[11]

Experimental Section

A natural calcite crystal was cleaved along its $(10\bar{1}1)$ cleavage planes to yield slices 1–2 mm thick and about 7 mm in diameter. Spectroscopic analysis showed the principal metallic impurities of the crystal to be 0.08% Mn, 0.002% Mg, 0.005% Sr, 0.001% Cu, <0.005% Fe, <0.001% Ag, and <0.001% Ba.

Samples were suspended by a silica fiber from an arm of a Cahn R.G. electrobalance, which had been calibrated with a 50 mg weight. The balance range used had a sensitivity of ~10 μg. The vacuum chamber was constructed of stainless steel with internal tungsten hairpin-shaped heating elements connected in parallel. To reduce temperature gradients and contamination of the samples by condensable products of reaction of CO_2 with the tungsten filaments, a platinum cylinder 3 cm in diameter and 10 cm long was placed around the sample. Temperatures were measured with a Pt–Pt—10% Rh thermocouple placed with its junction immediately below the sample. Temperatures read with this thermocouple were corrected for the difference between its temperature and that of a similar thermocouple that was placed for a calibration run in the position subsequently occupied by the calcite crystals.

The sample chamber could be evacuated to a residual pressure of $<3 \times 10^{-4}$ Pa during decomposition. When runs were to be made in CO_2, the diffusion pump was turned off and CO_2 was held at a steady-state level by adjusting a leak valve. Pressures were measured with an ion gauge.

Results and Discussion

In a previous study made with a calcite crystal, which was masked so that only part of a single face was exposed, the decomposition rate remained constant until about 75% of the crystal had decomposed.[1] In the present study, decomposition occurred over the entire crystal surface. To ensure that measurements were dependent only upon CO_2 pressure and not upon the extent of reaction, decomposition rates were measured under vacuum for calcite slices of two different thicknesses (Figure 1). These runs show that some 50% of the crystals could be decomposed in vacuum before the rates of decomposition decreased significantly.

Figure 2 compares kinetic data obtained as a function of temperature under vacuum in the present study to data of two other studies in this laboratory.[1,4] The kinetic data are reported in terms of the pressure inside an ideal effusion orifice that would yield the flux of CO_2 that is found to leave the crystals. These equivalent pressures are calculated from the Hertz–Knudsen–Langmuir equation $P_L = J(2\pi MRT)^{1/2}$, where J is the observed molar flux density, P_L is the equivalent pressure, M is the molecular weight of the gas, R is the gas constant, and T is the absolute temperature.

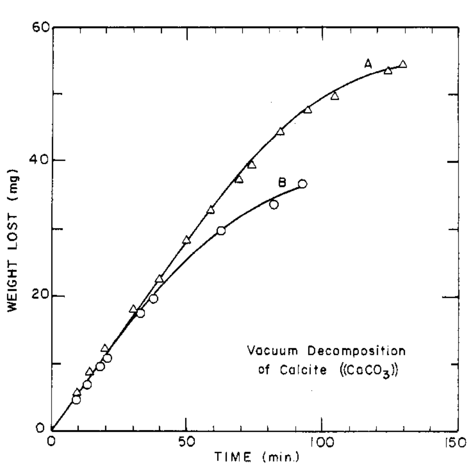

Figure 1. Decomposition rates measured as a function of time for two $CaCO_3$ crystals that differed by about a factor of 2 in mass: curve A, larger crystal; curve B, smaller crystal.

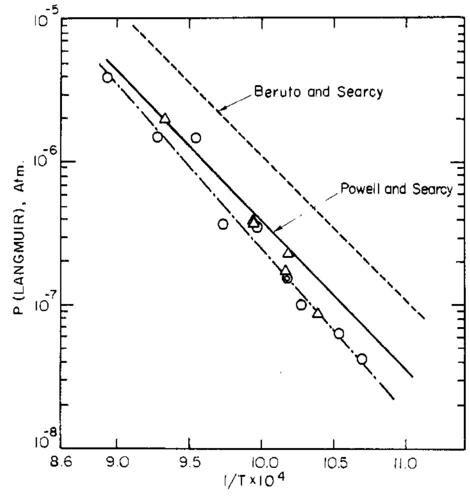

Figure 2. Values found for the CO_2 flux from $CaCO_3$ decomposed under vacuum. The open circles are data collected in a single run under vacuum (the line–··–is a least-squares fit for this run). The triangles are initial points measured in isothermal runs in which CO_2 background pressures were varied. The dashed line is from Beruto and Searcy[1] and the solid line is from Powell and Searcy.[4]

The line described in the figure caption as a least-squares fit to data measured in the present study was calculated from data obtained in a single heating under vacuum which yielded the points shown by open circles. The points marked by triangles were measured under vacuum at the beginning of isothermal runs at varied CO_2 pressures. Data of Powell and Searcy are believed to be subject to the least experimental error.[4] The differences in fluxes reported in the three investigations may result from calibration errors, but may also be a consequence of as-yet unidentified effects of small differences in composition or crystal imperfections on the rates.

For calcite decomposition, these three studies agree in showing that the ratio of the apparent decomposition pressure to the equilibrium decomposition pressure is $P_L/P_{eq} \simeq 10^{-5}$ (not 10^{-3}, as misstated in ref 1). The apparent enthalpy of activation for the decomposition calculated from the temperature dependence of $\ln P_L = -(\Delta H^*/RT) + (\Delta S^*/R)$, using P_L values measured in the isothermal run of this study, is 220 ± 20 kJ. The best value that can at present be set for ΔH^* is 209 ± 12 kJ.[4]

Both Hyatt et al. and Cremer and Nitsch reported that the rate of decomposition of $CaCO_3$ is a parabolic function

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[10] G. Bertrand, *J. Phys. Chem.*, **82**, 2536 (1978).

[11] A. W. Searcy and D. Beruto, *J. Phys. Chem.*, **82**, 2537 (1978).

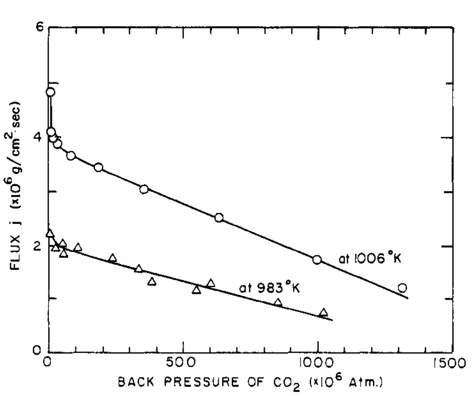

Figure 3. Flux of CO_2 plotted vs. P_{CO_2} at 983 and 1006 K.

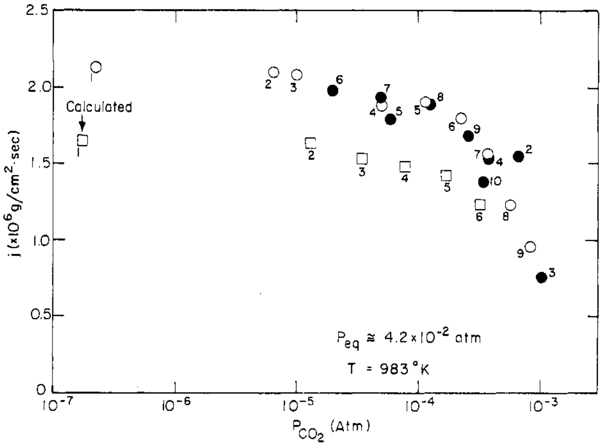

Figure 4. Flux of CO_2 vs. log P_{CO_2} measured in three runs at 983 K. Points numbered in order measured in each run. The point marked "calculated" is interpolated from our measurements of Figure 2.

of P_{CO_2}. It is only possible to make qualitative comparisons of the pressure dependence found for rates in the present study to their data, because the Hyatt data are reported only as points on a small scale plot, and Cremer and Nitsch worked with powders.

Figure 3 shows the fluxes of CO_2 measured as functions of the pressure of CO_2 at 983 and at 1006 K in the present research. The sharp change in slope might be interpreted as being consistent with a parabolic dependence of flux on CO_2 pressure, but at higher CO_2 pressures the dependence of flux on pressure might more reasonably be described as linear. Furthermore, in the low-pressure range where $P_L < P_{CO_2} < 10^3 P_L$ the flux remains within about a factor of 2 of the flux produced under vacuum (Figures 4–7).

Points of these figures are numbered in the sequence in which the data were collected. The point marked "calculated" is a value from the plot of rates under vacuum (Figure 1).

When runs were initiated under vacuum and the pressures were progressively raised, the plots that result are relatively smooth and reproducible; but fluxes measured near the bend in these fluxes vs. log P_{CO_2} plots are sensitive to sample history.

The sensitivity of flux to history probably results because different CO_2 pressure sequences result in different CaO particle sizes at the reaction interface. Ewing et al. have shown that the surface area of the CaO produced in calcite *powder* composition decreases when the CO_2 pressure exceeds $\sim 0.1 P_{eq}$.[12] This surface area decrease implies that the CaO particles and pore diameters at the reaction front are increased as P_{CO_2} approaches P_{eq}. The CaO surface areas produced by decomposition of large calcite crystals probably have a similar dependence on CO_2 pressures. Variation in CaO particle size could influence the condensed phase reaction rates by varying the condensed phase diffusion distances and by varying strain near the interface. Variations in strain would in turn change the free energy barrier to condensed phase diffu-

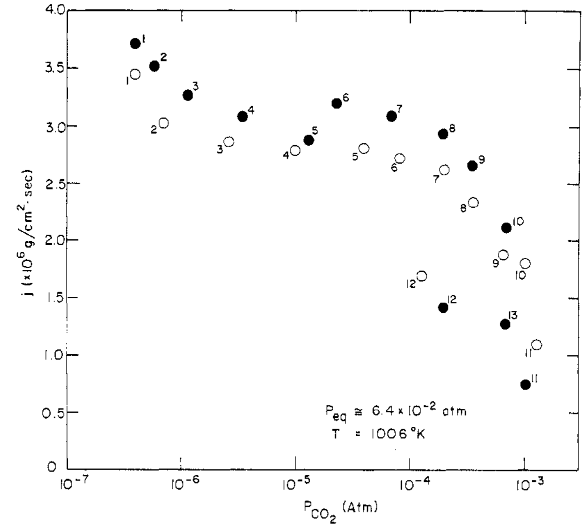

Figure 5. Flux of CO_2 vs. log P_{CO_2} at 1006 K. Points numbered in order measured.

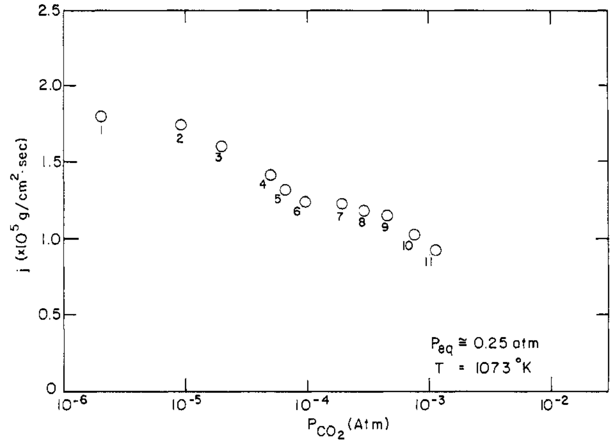

Figure 6. Flux of CO_2 vs. log P_{CO_2} at 1073 K. Points numbered in order measured.

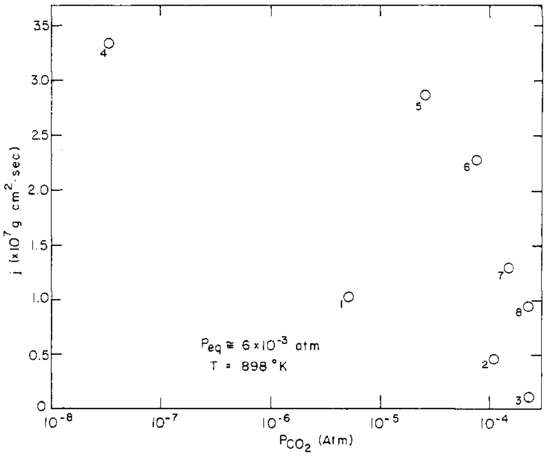

Figure 7. Flux of CO_2 vs. log P_{CO_2} at 898 K. Points numbered in order measured.

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[12] J. Ewing, D. Beruto, and A. W. Searcy, *J. Am. Ceram. Soc.*, **62**, 580 (1979).

sion, and perhaps might also change the barrier to surface or interfacial steps.

Whether or not the sensitivity of flux to sample history is neglected, it is apparent that in the pressure range from $P_{CO_2} < P_L \simeq 10^{-5}P_{eq}$ to $P_{CO_2} \simeq 10^{-2}P_{eq}$, where the CO_2 flux against the sample exceeds the decomposition flux by a factor of $\sim 10^3$, the flux is essentially independent of P_{CO_2}. Thus, in this regime, the molar flux density J is given by an equation of the form

$$J = k(P_{eq} - P_{CO_2}) \simeq kP_{eq} \qquad (1)$$

The model of Searcy and Beruto yields this expression for the pressure dependence when the rate-limiting process is either solid-state diffusion of CO_2 or a surface step for CO_2.[6] That model did not consider the possibility that the solid component of a decomposition reaction might be displaced from the reactant phase to the product solid phase by a cooperative process—such as twinning or shear—in which groups of atoms or ions move simultaneously. In $CdCO_3$ decomposition, the CdO phase probably forms by twinning in volume elements of the $CdCO_3$ after diffusion of all or part of the CO_2 from those elements makes them sufficiently unstable.[10,13,14] A similar process can be expected in $CaCO_3$ decomposition.[10,13,14]

If so, because cooperative processes are very rapid, the rate-limiting process must be diffusion of CO_2 from the $CaCO_3$ volume elements near the advancing reaction front or a surface step in the desorption of CO_2, and the predicted rate equations then have the same form as eq 1: At low CO_2 pressures, condensed-phase diffusion of CO_2 (perhaps as countercurrents of CO_3^{2-} and O^{2-} ions), or a surface step of CO_2, e.g., decomposition of CO_3^{2-} to O^{2-} and adsorbed CO_2, is the rate-limiting process in $CaCO_3$ decomposition.[10]

The possibility that the *final* step of CO_2 desorption is rate limiting can be eliminated by comparison of the apparent activation entropy, calculated when desorption is assumed to be rate limiting, to the standard entropy of the reaction $CaCO_3(s) = CaO(s) + CO_2(g)$. Even if CaO is produced in a thermodynamically active state, its entropy would be unlikely to increase by more than 8–12 J/(mol deg) over the entropy of normal CaO. By analogy with an analysis given elsewhere for congruent vaporization,[15] if desorption of CO_2 were rate limiting the transition state would have properties close to those of the separate CaO solid phase plus CO_2 gas, and the apparent entropy of activation should be close to the entropy of the equilibrium decomposition reaction. The apparent entropy of activation ΔS^* can be calculated from the measured apparent activation enthalpy[4] and the values of P_L in Figure 2 by means of the relation $\ln P_L = -\Delta H^*/RT + \Delta S^*/R$. If P_L from ref 4 at 1000 K is used, ΔS^* is calculated to be 84 ± 12 J/(mol deg) (20 ± 3 cal/(mol deg)), which is much lower than the standard entropy, 147 J/(mol deg) (35 cal/(mol deg)) at 1000 K.

The present study shows that the mechanism for calcite decomposition is different at $P_{CO_2} > \sim 10^{-2}P_{eq}$ than in the low-pressure range, but the dependence on P_{CO_2} at high CO_2 pressures is not parabolic as concluded from earlier studies over more limited pressure ranges. Shukla and Searcy will report a more detailed study[16] of the influence of high relative CO_2 pressures on calcite decomposition rates.

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Franck–Condon Model for Collinear Reactive Systems. Factorization of the Reactive Vibrational Amplitudes and Probabilities

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This work presents a model for collinear reactive scattering which, under certain conditions, becomes a Franck–Condon-type model. Further analysis leads to the factorization of the reactive vibrational amplitudes (and probabilities) which yields two *linearly dependent variables* for each final vibrational state. From the parameters of the straight line, the ratio of the two fundamental frequencies of the oscillators and their relative coordinate shift can be obtained. The model is applied to the two isotopic reactions $H(D) + Cl_2 \rightarrow H(D)Cl + Cl$.

Introduction

The Franck–Condon (FC) model for collinear reactive scattering and the two isotopic reactive systems

$$H(D) + Cl_2 \rightarrow H(D)Cl + Cl \qquad (1)$$

are closely related; indeed, the quantum-mechanical vibrational distributions obtained for these systems led to the FC model.[1] Since then, the FC model has been applied in different forms to this and other systems, with varying degrees of success,[2-7] and the $H + Cl_2$ system has

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