ε = voidage of the porous product solid [—]

Literature Cited

- 1) Bellman, R., E. S. Lee and K. M. Wang: *Chem. Eng. Sci.*, **32**, 1051 (1977).
- 2) Bischoff, K. B.: *ibid.*, **18** 711 (1963).
- 3) *idem*: *ibid.*, **20**, 783 (1965).
- 4) Boley, B. A.: *J. Math. Phys.*, **40**, 300 (1961).
- 5) Bowen, J. R.: *Chem. Eng. Sci.*, **20**, 712 (1965).
- 6) Gupta, S. C. and A. K. Lahiri: *Int. J. Eng. Sci.*, **7**, 401 (1979).
- 7) Ockendon, J. R. and W. R. Hodgkins (Ed.): "Moving Boundary Problems in Heat Flow and Diffusion", Clarendon Press, Oxford (1975).
- 8) Portnov, I. G.: *Soviet Phy. Dokl.*, **7**, 186 (1962).
- 9) Taniguchi, S., M. Ohmi and M. Yamada: *Trans. of Iron and Steel Inst. Japan*, **14**, 214 (1974).
- 10) Van Der Pol, B. and H. Bremmer: "Operational Calculus Based on the Two-sided Laplace Integral", Cambridge (1955).
- 11) Yoshida, K., D. Kunii and F. Shimizu: *J. Chem. Eng. Japan*, **8**, 417 (1975).

PHOTOCHEMICAL KINETICS IN INFRARED LASER SEPARATION OF BORON ISOTOPES

KAZUO TAKEUCHI, OSAMU KURIHARA AND RYOHEI NAKANE
The Institute of Physical and Chemical Research, Wako, Saitama 351

Introduction

Since the invention of lasers, their extremely high beam intensity and monochromaticity have been successfully applied to isotope separation^{5,6}. When the absorption cross-sections of this monochromatic light source are considerably different for two different isotope compounds (in the most desirable case, one of them is null), monochromatic light in UV, visible and IR regions can excite only one of them electronically or vibrationally. And when dissociation or bi-molecular reaction follows the excitation, the molecule containing a particular isotope can be converted into other substances which can be easily separated from the unreacted compound containing a different isotope, using conventional separation techniques.

When the pulsed IR laser has intensity in the order of MW/cm², polyatomic molecules tend to be highly vibrationally excited, absorbing more than one photon. The excited molecules either react with the second gas, called the acceptor, or dissociate into radicals. For the second case, there are two possibilities. Molecules such as SF₆, CCl₄ and CCl₂F₂ tend to form stable final products, while molecules such as BCl₃ and SiF₄ do not, requiring the acceptor for isotope enrichment.

Today, it is well known that such infrared laser isotope separation has many advantages over that in UV or visible region⁸) for such practical applications as uranium enrichment and deuterium/tritium separation. Our object is to find the simplest and most

useful expressions in kinetics that can be used for scale-up purposes based on the minimum number of experimental results.

For this goal, the reaction BCl₃ + H₂S is adopted as a model reaction, since BCl₃ has isotopically selective absorption peaks in the wavelength range of highly efficient CO₂ lasers.

1. Experimental

A schematic diagram of experimental apparatus is shown in **Fig. 1**. A transversely excited atmospheric pressure (T.E.A.) CO₂ laser (Lumonics 103-2) was operated with gas mixing ratio of 0.91 : 0.09 : 0.00 for He : CO₂ : N₂. The laser can emit maximum 1.4 J per pulse at a repetition rate of 0.7 Hz. Nitrogen was not used as laser gas, to avoid possible thermal scrambling caused by the tail of the pulse such as reported by Freund⁹). The original beam pattern was roughly rectangular, 3 cm × 3.5 cm. Teflon irises were used to eliminate the inhomogeneous portion of the beam. Then the beam was focussed using a KRS-5 lens (f=30 cm) at the center of the cross-shaped cell, which was 30 cm long in irradiation direction and 5 cm long for IR spectroscopic analysis. The reaction cell was made of Pyrex with four KBr windows (35φ × 5 mm). For all runs, concentrations of ¹¹BCl₃ and ¹⁰BCl₃ were measured by a double-beam IR spectrophotometer (JASCO A102) using absorption peaks at 956 cm⁻¹ and 995 cm⁻¹, respectively. Pulse energy measurements were made before and after passage through the cell by a disk calorimeter (Sciencetech 361). The reaction cells were dried by heating for 48 hours under vacuum before use to avoid non-selective thermal

Received September 7, 1979. Correspondence concerning this article should be addressed to K. Takeuchi.

Fig. 1 Schematic diagram of experimental apparatus

hydrolysis of boron trichloride. BCl₃ gas containing naturally abundant 20% ¹⁰BCl₃ and 80% ¹¹BCl₃ of 99.9% purity and H₂S gas of 99% purity were supplied by Matheson and then vacuum-distilled for further purification.

The laser line was tuned at P (20) line at 944.2 cm⁻¹ so that it might be in resonance with ¹¹BCl₃ ν₃ asymmetric stretching mode. Initial pressures for BCl₃ and H₂S were 0.27 kPa and 1.33 kPa, respectively.

2. Results and Discussion

Figure 2 shows a typical example of IR spectra before and after irradiation. Resonant ¹¹BCl₃ is more reacted than non-resonant ¹⁰BCl₃.

Figure 3 shows that the concentration changes for ¹¹BCl₃ and ¹⁰BCl₃ obey pseudo-first order kinetics as given by Eq. (1) since the plot of -ln(1-X) vs. *t* is linear, where *X* is the fractional conversion of each isotopic compound and *t* is the number of pulses.

$$1 - X_A = \exp(-d_A t) \quad (1a)$$

$$1 - X_B = \exp(-d_B t) \quad (1b)$$

Hydrogen sulfide used as the acceptor is always in excess. The slopes *d_A* and *d_B* give the overall reaction rate constants, and the ratio of the two slopes in Fig. 2 is defined as the selectivity *S*.

In infrared laser isotope separation, the relation corresponding to temperature dependence of thermal reaction rate constants is the pulse energy dependence of *d_A* and *d_B*. We shall discuss this subject, as most physicists do, by utilizing a power law expression such as

$$d_A = A' E_0^m \quad (2)$$

Figure 4 shows the pulse energy dependence of *d_A* and *d_B* based on Eq. (2). While *d_A* is proportional to *E₀*^{0.90}, *d_B* is proportional to *E₀*^{0.68}, indicating that selectivity increases with *E₀*.

Dependence of the reaction rate constants on incident pulse energy *E₀*, fluence Φ and beam intensity *I* has been extensively studied for other molecules such as SF₆. The values for *m* in the relation *d_A* ∝ Φ^{*m*} range from 1.01 to 1.96 and 1.5 to 2.77 in the relation *d_A* ∝ *E₀*^{*m*} for SF₆^{1,2,4,7)}. Since the experimental error

Fig. 2 Examples of typical IR spectra of BCl₃ (0.27 kPa) before irradiation (left) and after irradiation of 6000 pulses (right) at 944.2 cm⁻¹

Fig. 3 Plot of fractional unconversion (1-X) = *N/N₀* vs. pulse number *t* for resonant ¹¹BCl₃ and non-resonant ¹⁰BCl₃

Fig. 4 Dependence of resonant reaction rate constant *d_A* and non-resonant reaction rate constant *d_B* on incident pulse energy *E₀*

associated with the determination of *m* is estimated to be ±15%, the interpretation of linear dependence of *d_A* on *E₀* (*d_A* ∝ *E₀*¹) shown by Gower *et al.*⁴⁾ for multiphoton dissociation of SF₆ can be applied to this case. That is, the local reaction rate constant *k* in a small segment of the irradiated volume can be related linear-

Fig. 5 Experimentally obtained enrichment factor for the unreacted β_{res} and that for the product β_{prod} as function of pulse number t in comparison with theory (solid lines)

ly to spatially and chronologically variable beam intensity I ($k \propto I^1$). Therefore the pulse energy dependence for a resonant molecule is expected to be independent of irradiation geometry.

On the other hand, that for a non-resonant substance is more complex since d_B is the result of spatial and chronological averaging of the non-linear dependence on I .

This is due to the fact that we start from a crude parallel reaction model such as shown in scheme (I) rather than a more realistic model such as scheme (II) as shown below.

Without further investigation of the kinetics of v-v excitation transfer $A^* + B \rightarrow A + B^*$, the pulse energy dependence of d_B cannot be fully understood.

Nevertheless, when Eqs. (1a) and (1b) hold, the enrichment factors β_{res} for the unreacted and β_{prod} for the product can be written as

$$\beta_{\text{res}} \equiv \frac{(N_B/N_{B0})}{(N_A/N_{A0})} = \exp\left(\frac{S-1}{S} d_A t\right) \quad (3)$$

$$\beta_{\text{prod}} \equiv \frac{(N_{A0} - N_A)/N_{A0}}{(N_{B0} - N_B)/N_{B0}} = \frac{1 - \exp(-d_A t)}{1 - \exp(-d_B t)} \quad (4)$$

From Eq. (3), it is easily understood that β_{res} can be increased exponentially as t is increased. But for the sake of realistic isotope separation where the abundance of the desired isotope is low, β_{prod} is more important. Simple calculation shows that β_{prod} decreases monotonically as t increases. The maximum value for β_{prod} is equal to S at $t=0$ where $S = d_A/d_B$.

The same data in Fig. 3 is reproduced in Fig. 5 with β_{res} and β_{prod} to illustrate the process of batch

isotope enrichment as given by Eqs. (3) and (4). This also illustrates the importance of the finding of the phenomenological pseudo-first order expressions such as Eqs. (1a) and (1b) since it leads to such simple expressions for β_{res} and β_{prod} as in Eqs. (3) and (4), though intrinsic mechanisms for multiphoton excitation and chemical reaction accompanied by resonant excitation transfer among many vibrational levels causing scrambling can be quite complex.

Conclusion

The kinetic model for infrared laser isotope separation is presented to elucidate the results of batchwise experiments with a series of pulsed irradiation. Overall kinetics was found to obey the pseudo-first order parallel reaction scheme for resonant $^{11}\text{BCl}_3$ and non-resonant $^{10}\text{BCl}_3$.

This enables us to express the enrichment factors for the unreacted and the product in simple fashion as functions of the resonant reaction rate constant d_A and the selectivity S .

Acknowledgment

The authors are grateful to Professor Susumu Namba and his co-workers in the Semiconductor Laboratory of the Institute of Physical and Chemical Research for their kind permission for our use of the CO_2 T.E.A. laser and numerous valuable suggestions.

Nomenclature

d_A	= overall reaction rate constant for resonant molecule A	[-]
d_B	= overall reaction rate constant for non-resonant molecule B	[-]
E_0	= incident pulse energy	[J]
I	= beam intensity	[W/cm ²]
k	= local reaction rate constant	[s ⁻¹]
N_A	= concentration of A after irradiation	[mol/cm ³]
N_B	= concentration of B after irradiation	[mol/cm ³]
N_{A0}	= concentration of A before irradiation	[mol/cm ³]
N_{B0}	= concentration of B before irradiation	[mol/cm ³]
S	= d_A/d_B = selectivity	[-]
β_{res}	= enrichment factor for unreacted gas as defined by Eq. (3)	[-]
β_{prod}	= enrichment factor for product as defined by Eq. (4)	[-]
Φ	= fluence	[J/cm ²]

Literature Cited

- 1) Ambartsumian, R. V. *et al.*: *Sov. Phys. JETP*, **42**, 993 (1975).
- 2) Fuss, W. and T. P. Cotter: *Appl. Phys.*, **12**, 265 (1977).
- 3) Freund, S. M. and J. J. Ritter: *Chem. Phys., Lett.*, **32**, 255 (1975).
- 4) Gower, M. C. *et al.*: *Opt. Comm.*, **20**, 123 (1977).
- 5) Kimel, S. and S. Speiser: *Chem. Review*, **77**, 437 (1977).
- 6) Letokhov, V. S.: *Physics Today*, **May**, 23 (1977).
- 7) Lyman, J. L. *et al.*: *J. Chem. Phys.*, **67**, 4545 (1977).
- 8) Moore, C. B., "Chemical and Biochemical Applications of Lasers", vol. III, p. 122, Academic Press (1977).