CHEMISTRY LETTERS, pp. 343-346, 1979. Published by the Chemical Society of Japan

A TRIAL MONTE CARLO TRAJECTORY CALCULATION OF THE RATE CONSTANTS FOR THE REACTIONS H_2+I AND H_2+I_2

Ryuichi MINAMI and Takayuki FUENO
Department of Chemistry, Faculty of Engineering Science,
Osaka University, Osaka 560

A thermal rate constant k(T) is computed by the conditional Monte Carlo trajectory method. Characteristic of this method is that it reduces the trajectory data directly to k(T) without explicit calculation of the cross sections. Reaction systems $H_2+I \longrightarrow HI+H$ and $H_2+I_2 \longrightarrow 2HI$ are studied as examples.

The conventional numerical calculation of reaction rate by the Monte Carlo method generally requires a large number of trajectory data. In the standard Monte Carlo procedure (i.e. analog Monte Carlo), some cross sections $\sigma(E_t,j,v)$ are first computed at relative translational energy E_t in a rotation-vibrational state (j,v) of reactants. Then a thermal reaction rate constant k(T) is obtained by numerically averaging the cross sections multiplied by the relative velocity over thermal distribution densities of (E_t,j,v) at a given temperature T. The number of cross sections corresponds to that of sets of (E_t,j,v). If the number of necessary sets for the above calculation is small like as the H+H_2 system, the total amount of trajectories may be within the limits of that procedure. However, it is scarcely possible to encounter this luck. The vibration-rotational energy levels of a popular diatomic molecule are very close just as the I_2 molecule. In the conventional studies, this difficulty has been escaped by calculating the rotationally averaged cross sections $\sigma(E_t,v)$ at one temperature.$^{1)}$ This approach reduces the number of sets of (E_t,j,v), though it neglects the rotational temperature effect on the reaction rate. We attempt to avoid these difficulties as below.

The rate $k_{a,b}(T)$ for a reaction channel such that an initial reaction system <u>a</u> (AB+C or AB+CD) goes to a final product system <u>b</u> can be represented by$^{1,2)}$

$$k_{a,b}(T) = N_A(2/k_BT)^{3/2}(1/\pi\mu)^{1/2}Q_{vib}{}^{-1}Q_{rot}{}^{-1}\sum_{v,j} g_j(2j+1)\exp(-(E_v+E_j)/k_BT) \times \int_0^\infty \sigma_{a,b}(E_t,j,v)\exp(-E_t/k_BT)E_t dE_t, \qquad (1)$$

where N_A is Avogadro's number, k_B is the Boltzmann constant, μ is the reduced mass of the <u>a</u> system, Q_{vib} and Q_{rot} are the partition functions for the vibration and the rotation system characterized by typical quantum numbers v and j, respectively, and g_j is the statistical weight of rotational state j. $\sigma_{a,b}(E_t,j,v)$ is the cross section of channel $\underline{a} \longrightarrow \underline{b}$ and includes some integrals over impact parameter and initial phases of internal motions of reactants. Then Equation (1) seems to be directly computable by the analog Monte Carlo trajectory method. However, this attempt meets with failure for many interesting reactive collisions. Most of collisions have the smaller energy than the threshold one and are not reactive. Therefore the analog Monte Carlo method can not give accurate results.

We have introduced the conditional Monte Carlo method[3] into the computation of reaction rate i.e. Equation (1). An expected value of the probability Pr(x) observing a variables x is expressibles as

$$\int_0^\infty \Pr(x)G'(x)dx = \int_0^1 \Pr(x)dG(x), \tag{2}$$

where G(x) and G'(x) are the natural distribution and density functions, respectively. The above integral can be transformed by the conditional distribution function F(x) and estimated by applying the conditional Monte Carlo method as follows.

$$\int_0^1 \Pr(x)\,\frac{G'(x)}{F'(x)}\,dF(x) = \frac{1}{N}\sum_{i=1}^{N}\Pr(x_i)\,\frac{G'(x_i)}{F'(x_i)}\,, \tag{3}$$

where x_i is i-th variable in N-samplings of the conditional Monte Carlo method and F'(x) is the conditional density function. Equation (3) represents the possibility that a natural distribution is modulated to a conditional distribution for the purpose of computing with less numerous samples. This modulation has been useful to choose an impact parameter.[1,4] In reality, the majority of trajectories lead to a nonreactive channel because they have the smaller relative translational energy than the threshold one at our objective temperature. Therefore, the conditional Monte Carlo integral procedure can bring forth proper values of the reaction rate constants with fewer trajectories than can the analog Monte Carlo.

We have computed the rates of reactions H_2+I ⟶ HI+H and H_2+I_2 ⟶ 2HI as examples. The conditional distribution functions that we used to choose impact parameter b and the relative translational energy E_t are listed in Table 1.

Table 1. Conditional distribution functions

Variable	Distribution function F
Impact parameter b	$F(b) = \begin{cases} b/b_{max} & \text{for } 0 \le b < b_{max}{}^{a)} \\ 1 & \text{for } b_{max} \le b \end{cases}$
Relative translational energy E_t	$F(E_t) = \begin{cases} E_t/E_{t,max} & \text{for } 0 \le E_t < E_{t,max}{}^{a)} \\ 1 & \text{for } E_{t,max} \le E_t \end{cases}$

a) Employed values, b_{max}: 5.5 a.u. for H_2+I and 8.0 a.u. for H_2+I_2,
$E_{t,max}$: 50 ~ 100 kcal/mol.

The initial phase of every intramolecular motion, the rotational quantum number of each molecule, and the vibrational quantum number of I_2 were all determined by the analog Monte Carlo method. The vibrational quantum number of H_2 was fixed. Each distribution function G of the rotation-vibrational energy levels was characterized by thermal equilibrium conditions. After the initial values of a system having been selected at a given temperature T, each trajectory was computed by the standard technique.[5)] The trajectory calculations were performed on a FACOM M-190 computer, using the fifth-order Adams-Moulton routine with a time increment of 2×10^{-16} s. About 2000 trajectories for H_2+I and about 1000 trajectories for H_2+I_2 were run at carried out by the conditional Monte Carlo integration procedure, to obtain the thermal reaction rate k(T,v) at initial vibrational quantum number v of H_2. Figure 1 shows the calculated values of k(T,v). The potential surfaces employed in this study are identical with those given in references 1 and 5.

The overall thermal rate constant $k_o(T)$ at T is given by

$$k_o(T) = Q_{vib}{}^{-1}\sum_{v} k(T,v)\exp(-E_v/k_BT), \tag{4}$$

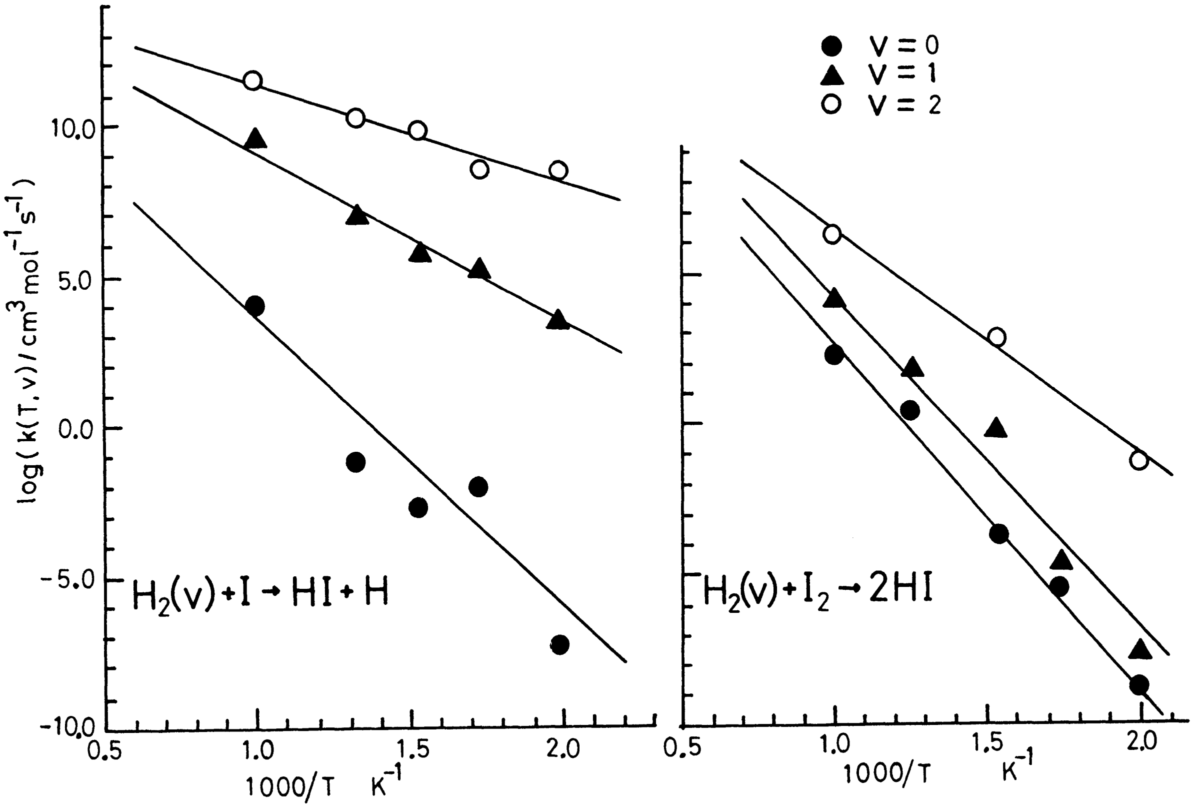

Fig. 1. Arrhenius plots of k(T,v). The points (●, ▲ and ○) represent the calculated values of k(T,v). The straight lines are the least-squares ones.

where Q_{vib} is the partition function for the vibration system of H_2. Arrhenius plots of $k_0(T)$ are shown in Figure 2. The slope of the Arrhenius plot for $H_2+I \longrightarrow HI+H$ yields an activation energy 35.2 kcal/mol, which compares well with 34.2 kcal/mol obtained by Porter et al.$^{1)}$ For the reaction $H_2+I_2 \longrightarrow 2HI$, an activation energy of 52.6 kcal/mol was obtained.

It has been supposed that the procedure by which the reaction rate constants are computed directly from the data of trajectories without calculating the cross sections appears to be useful. However, it could not be performed by the analog Monte Carlo method. Consequently, we developed it by use of the conditional Monte Carlo method. The results of two example calculations are in fair agreement with the Arrhenius law. This indicates that the present method is available for the calculation of the reaction rate constant. Furthermore, we may expect its application to complex collisions of large polyatomic molecules to be particularly fruitful.

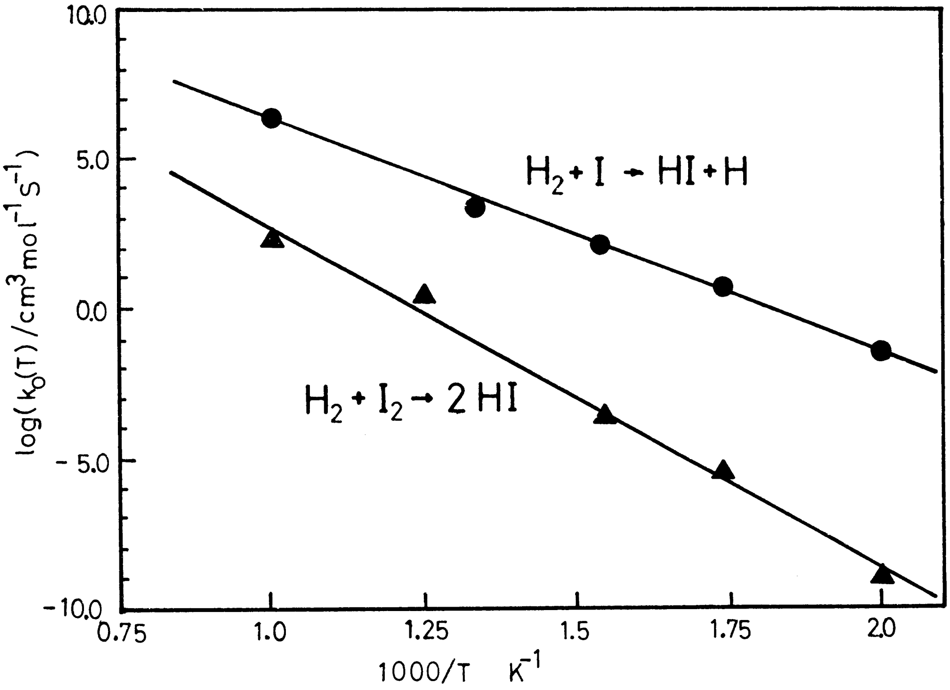

Fig. 2. Arrhenius plots of $k_0(T)$. The points (● and ▲) represent the calculated values of $k_0(T)$.

References

1) R.N.Porter, L.B.Sims, D.L.Thompson, and L.M.Raff, J.Chem.Phys., 58 2855 (1973).
2) M.Karplus, R.N.Porter, and R.D.Sharma, ibid., 43 3259 (1965).
3) O.Miyatake and T.Nakayama, "Monte Carlo Method," Nikkan Kogyo Shinbun, Tokyo (1966), Appendix 1. Conditional Monte Carlo Method.
4) C.A.Parr, J.C.Polanyi, and W.H.Wong, J.Chem.Phys., 58 5 (1973).
5) L.M.Raff, D.L.Thompson, L.B.Sims, and R.N.Porter, ibid., 56 5998 (1972).

(Received November 21, 1979)