Calculation of the Reaction Cross Section from a Rate Constant by the Method of Steepest-Descent

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Communicated November 5, 1970

ABSTRACT The reaction cross section of a bimolecular reaction has been calculated from the corresponding rate constant by the inverse Laplace transform. In carrying out the inverse Laplace transform, the method of steepest-descent has been used. As applications, the reaction cross sections for the rate constant of $k(T) = k' T^n e^{-E_0/kT}$ and for the rate constant of the absolute reaction rate theory have been calculated. The computation of the energy density function associated with the definition of the weighted-average cross section has also been discussed.

It has been shown [1, 2] that from the collision theory of chemical reactions, the rate constant of a bimolecular reaction based on the assumptions of thermal equilibrium for the translational degrees of freedom and for the internal degrees of freedom of the reactant molecules can be expressed as

$$k(T) = \frac{1}{Q_{ab}^{\text{int}}(T)} \sum_{ij} \sum_{kl} \exp \{ -\beta(\epsilon_{ai} + \epsilon_{bj}) \} k_{ij}^{kl}(T) \quad (1)$$

where $\beta = \frac{1}{kT}$, $Q_{ab}^{\text{int}}(T)$ represents the product of the internal partition functions of reactants *A* and *B*, and $k_{ij}^{kl}(T)$ is the detailed rate constant of the reaction from the reactants in (*i,j*) states to the products in (*k,l*) states. This detailed rate constant is related to the chemical-reaction cross section $\sigma_{ij}^{kl}(E)$ as follows:

$$k_{ij}^{kl}(T) = \sqrt{\frac{8\beta^3}{\pi\mu}} \int_0^\infty \sigma_{ij}^{kl}(E) E e^{-\beta E} dE \quad (2)$$

where *E* and μ represent the relative translational energy and the reduced mass of the collision partners, respectively. If the internal states of the reactant molecules do not affect the probability of reaction, Eq. (1) becomes

$$k(T) = \sqrt{\frac{8\beta^3}{\pi\mu}} \int_0^\infty \sigma(E) E e^{-\beta E} dE. \quad (3)$$

Thus we can see that the rate constants are related to the chemical-reaction cross section by the Laplace transformation. Several quite general functional forms of the reaction cross section $\sigma(E)$ have been studied by LeRoy [3] and Menzinger and Wolfgang [4] by using Eq. (3). In this investigation, we shall calculate the reaction cross section by carrying out the inverse

Laplace transformation of the corresponding rate constant. For this purpose, the method of steepest-descent [5] will be used. The method of steepest-descent has recently been applied to the computation of the total number of quantum states and density of states of polyatomic molecules and ions by Lin *et al.* [6, 7], Hoare and Ruijgrok [8, 9], and Forst and Prášil [10]. To illustrate the method presented in this paper, the reaction cross section will be calculated for the bimolecular rate constants obtained from the absolute reaction rate theory [11], and for the rate constant of the form $k(T) = k' T^n e^{-E_0/kT}$. It will be shown that in general if the rate constant is of the functional form, $k(T) = k_0(T) e^{-E_0/kT}$, then the threshold energy exists and is equal to E_0 .

THEORY

First we consider the calculation of the reaction cross section from Eq. (3). If we let $K(\beta) = \sqrt{\pi\mu}/8\beta^{-3/2} k(\beta)$, then Eq. (2) can be written as

$$E\sigma(E) = \frac{1}{2\pi i} \int_{r-i\infty}^{r+i\infty} K(\beta) e^{\beta E} d\beta = \frac{1}{2\pi i} \int_{r-i\infty}^{r+i\infty} \exp \times [F(\beta)] d\beta \quad (4)$$

where $F(\beta) = \log K(\beta) + \beta E$ and γ is a constant greater than the real part of all the singularities of the integrand. Following Kubo [12, 13] and Hoare [9], we use the relation $\beta = \beta_1 + i\beta_2$ and expand $F(\beta)$ about the point β_1 in the imaginary direction,

$$F(\beta) = \sum_{k=0}^{\infty} \frac{1}{k!} F^{(k)}(\beta_1) (i\beta_2)^k. \quad (5)$$

If we choose β_1 to have the saddle point value β^* , which is determined by $F'(\beta^*) = 0$, or

$$E = \frac{3}{2} \frac{1}{\beta^*} - \frac{\partial \log k(\beta^*)}{\partial \beta^*} \quad (6)$$

Eq. (4) becomes

$$E\sigma(E) = e^{F(\beta^*)} \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp \left[\sum_{k=2}^{\infty} b_k (i\beta_2)^k \right] d\beta_2 \quad (7)$$

where $b_k = \frac{1}{k!} F^{(k)}(\beta^*)$,

$$b_k = (-1)^k \frac{3}{2k} \frac{1}{\beta^{*k}} + \frac{1}{k!} \cdot \frac{\partial^k \log k(\beta^*)}{\partial \beta^{*k}} \quad (k = 2, 3, 4, \dots) \quad (8)$$

For the purpose of discussing the high-order approximations of the steepest-descent method, we write Eq. (7) as (see ref. 9):

$$E\sigma(E) = e^{F(\beta^*)} \frac{1}{2\pi} \int_{-\infty}^{\infty} d\beta_2 \exp(-b_2 \beta_2^2) \sum_{k=0}^{\infty} B_k \beta_2^k \quad (9)$$

where the coefficients B_k are determined by combining Eqs. (7) and (9). Some particular values of B_k are:

$$B_0 = 1, B_1 = B_2 = 0, \quad B_3 = -ib_3, \quad B_4 = b_4, \\ B_5 = ib_5, \quad B_6 = -b_6 - \frac{1}{2} b_3, \text{ etc.} \quad (10)$$

The general relation between B_k and b_k has been obtained by Hoare [9]. The integrals in Eq. (9) for odd k vanish and the integration of Eq. (9) yields

$$E\sigma(E) = \sqrt{\frac{\mu}{32b_3\beta^{*3}}} k(\beta^*) e^{\beta^* E} \left[1 + \sum_{k=1}^{\infty} \frac{B_{2k}}{\sqrt{\pi}} \times \frac{\Gamma(k + 1/2)}{b_2^k} \right]. \quad (11)$$

The terms beyond the first represent the highest-order approximations in the steepest-descent method. The higher-order approximations of the steepest-descent method can be easily obtained [9]. In most cases the first-order approximation is sufficient. In the following we give the expression for $\sigma(E)$ up to the second-order approximation of the steepest-descent method [7, 9]:

$$\sigma_2(E) = \sigma_1(E) \left[1 + \left(\frac{3}{4} \cdot \frac{b_4}{b_2^2} - \frac{15}{16} \cdot \frac{b_3^2}{b_2^3} \right) + \dots \right] \quad (12)$$

where $\sigma_2(E)$ and $\sigma_1(E)$ represent, respectively, the second-order and first-order approximation expressions for $\sigma(E)$, i.e.,

$$\sigma_1(E) = \frac{1}{E} \sqrt{\frac{\mu}{32b_3\beta^{*3}}} k(\beta^*) e^{\beta^* E}. \quad (13)$$

The b_k 's are given in Eq. (8).

Next we consider Eq. (1), which can be written as

$$k(\beta) = \frac{1}{Q_{ab}^{\text{int}}(\beta)} \sqrt{\frac{8\beta^3}{\pi\mu}} \sum_{ij} \exp\{-\beta(\epsilon_{ai} + \epsilon_{bj})\} \times \int_0^{\infty} \sigma_{ij}(E) E e^{-\beta E} dE \quad (14)$$

where $\sigma_{ij}(E) = \sum_{kl} \sigma_{ij}^{kl}(E)$. The summations over i and j in Eq. (14) indicate that all the internal states of the reactants should be covered. If we let $\epsilon = E + \epsilon_{ai} +$

ϵ_{bj} , where ϵ represents the total energy, noticing that $\sigma(x) = 0$ for $x < 0$, we obtain [14, 15]

$$k(\beta) = \frac{1}{Q_{ab}^{\text{int}}(\beta)} \cdot \sqrt{8\beta^3/\pi\mu} \sum_{ij} \int_0^{\infty} \sigma_{ij}(\epsilon - \epsilon_{ai} - \epsilon_{bj}) \times (\epsilon - \epsilon_{ai} - \epsilon_{bj}) e^{-\beta\epsilon} d\epsilon. \quad (15)$$

By applying the inverse Laplace transformation to Eq. (15), we find

$$\sum_{ij} \sigma_{ij}(\epsilon - \epsilon_{ai} - \epsilon_{bj})(\epsilon - \epsilon_{ai} - \epsilon_{bj}) = \sqrt{\pi\mu/8} \cdot \frac{1}{2\pi i} \int_{\gamma-i\infty}^{\gamma+i\infty} k(\beta) Q_{ab}^{\text{int}}(\beta) \beta^{-3/2} e^{\beta\epsilon} d\beta. \quad (16)$$

The contour integral in Eq. (16) can again be integrated by using the method of steepest-descent. To the first-order approximation, Eq. (16) becomes

$$\sum_{ij} \sigma_{ij}(\epsilon - \epsilon_{ai} - \epsilon_{bj})(\epsilon - \epsilon_{ai} - \epsilon_{bj}) = \sqrt{\pi\mu/8\beta^{*3}} k(\beta^*) Q_{ab}^{\text{int}}(\beta^*) e^{\beta^* \epsilon} / \left\{ 2\pi \left[\frac{3}{2} \cdot \frac{1}{\beta^{*2}} + \frac{\partial^2}{\partial \beta^{*2}} \log k(\beta^*) + \frac{\partial^2}{\partial \beta^{*2}} \log Q_{ab}^{\text{int}}(\beta^*) \right] \right\}^{1/2} \quad (17)$$

where β^* is determined by

$$\frac{3}{2} \cdot \frac{1}{\beta^*} = \epsilon + \frac{\partial}{\partial \beta^*} \log k(\beta^*) + \frac{\partial}{\partial \beta^*} \log Q_{ab}^{\text{int}}(\beta^*). \quad (18)$$

The second-order approximation in this case can be calculated from Eq. (12) by noticing that

$$b_2 = \frac{1}{2} \left[\frac{3}{2} \cdot \frac{1}{\beta^{*2}} + \frac{\partial^2}{\partial \beta^{*2}} \{ \log k(\beta^*) Q_{ab}^{\text{int}}(\beta^*) \} \right] \quad (19-A)$$

$$b_3 = \frac{1}{3!} \left[-\frac{3}{\beta^{*3}} + \frac{\partial^3}{\partial \beta^{*3}} \{ \log k(\beta^*) Q_{ab}^{\text{int}}(\beta^*) \} \right] \quad (19-B)$$

and

$$b_4 = \frac{1}{4!} \left[\frac{9}{\beta^{*4}} + \frac{\partial^4}{\partial \beta^{*4}} \{ \log k(\beta^*) Q_{ab}^{\text{int}}(\beta^*) \} \right]. \quad (19-C)$$

Without knowing the functional dependence of the chemical-reaction cross section σ_{ij} on the energy, one cannot carry out the summations over the internal states of reactants given in Eqs. (15-17). However, it is convenient to define a weighted-average cross section $\bar{\sigma}(\epsilon)$ by [see refs. 14, 15]

$$\bar{\sigma}(\epsilon) = \frac{1}{W_E(\epsilon)} \sum_{ij} \sigma_{ij}(\epsilon - \epsilon_{ai} - \epsilon_{bj})(\epsilon - \epsilon_{ai} - \epsilon_{bj}) \quad (20)$$

where $W_E(\epsilon)$ represents the energy density function [14]

$$W_E(\epsilon) = \sum_{ij} (\epsilon - \epsilon_{ai} - \epsilon_{bj}) H(\epsilon - \epsilon_{ai} - \epsilon_{bj}). \quad (21)$$

$H(x)$ in Eq. (21) is the Heaviside step function; $H(x) = 1, x > 0, H(x) = 0, x < 0$. To the first-order approximation of the steepest-descent method, we obtain for

the average cross section $\bar{\sigma}(\epsilon)$

$$\bar{\sigma}_1(\epsilon) = \sqrt{\pi\mu/8\beta^{*3}} \cdot \frac{k(\beta^*)Q_{ab}^{\text{int}}(\beta^*)e^{\beta^*\epsilon}}{W_E(\epsilon) \left\{ 2\pi \left[\frac{3}{2} \cdot \frac{1}{\beta^{*2}} + \frac{\partial^2}{\partial\beta^{*2}} \log k(\beta^*) + \frac{\partial^2}{\partial\beta^{*2}} \log Q_{ab}^{\text{int}}(\beta^*) \right] \right\}^{1/2}} \quad (22)$$

The second-order approximation expression for $\bar{\sigma}(\epsilon)$ is exactly the same as that given in Eq. (12).

APPLICATION

As we can see from the previous section, any bimolecular rate constant can be easily inversely transformed to obtain the corresponding reaction cross section. As an application of calculating the cross section from the corresponding rate constant by using Eq. (3), we consider the rate constant of the following functional form:

$$k(T) = k'T^n e^{-E_0/kT} = k_0\beta^{-n} e^{-E_0\beta} \quad (23)$$

where n can be any number except $-3/2$. For the case of $n = -3/2$, there is no saddle point existing in the contour integral of Eq. (4). The cross section $\sigma(E)$ in this case, however, can easily be obtained directly from Eq. (4), which is,

$$\sigma(E) = k_0 \sqrt{\pi\mu/8} \cdot \frac{\delta(E - E_0)}{E} \quad (24)$$

where $\delta(E - E_0)$ is the delta function.

Now substituting Eq. (23) into Eq. (13), we obtain the expression for $\sigma(E)$ to the first-order approximation as

$$\sigma_1(E) = \frac{k_0}{E} \sqrt{\mu/32b_2\beta^{*3}} \beta^{*-n} \cdot e^{\beta^*(E-E_0)} \quad (25)$$

β^* , the saddle point value of β , is to be determined from Eq. (6), i.e.,

$$\beta^* = \frac{n + 3/2}{E - E_0} \quad (26)$$

Substituting Eq. (26) into Eq. (25) yields

$$\sigma_1(E) = \frac{k_0\sqrt{\mu}}{4E} \cdot \frac{(E - E_0)^{n+1/2}}{(n + 3/2)^{n+1}} e^{n+3/2} \quad (27)$$

which should be compared with the exact result,

$$\sigma(E) = \sqrt{\pi\mu/8} \cdot \frac{k_0}{\Gamma(n + 3/2)} \cdot \frac{(E - E_0)^{n+1/2}}{E} \quad (28)$$

where $\Gamma(x)$ is the gamma function. The difference between Eqs. (27) and (28) is simply in the replacement of $\Gamma(n + 3/2)$ by the approximate Stirling formula, $\Gamma(n + 3/2)/\sqrt{2\pi} (n + 3/2)^{n+1} e^{-n-3/2} \sim 1$.

From Eq. (12), we find the expression of $\sigma(E)$ to the second order approximation of the method of steepest-descent as

$$\sigma_2(E) = \sigma_1(E) \left[1 - \frac{1}{12} - \frac{1}{(n + 3/2)} + \dots \right] \quad (29)$$

As we can see from the above discussion, E_0 in the exponential term of the rate constant given in Eq. (23) becomes the threshold energy in the reaction cross section.

As an illustration of showing how to obtain the average reaction cross section from a rate constant, we consider the bimolecular rate constant obtained from the absolute reaction rate theory [11]. In this case, we have

$$k(\beta) = \kappa \frac{h^2}{2\pi\mu} \cdot \sqrt{\beta/2\pi\mu} \frac{Q_{+}^{\text{int}}(\beta)}{Q_{ab}^{\text{int}}(\beta)} e^{-\beta\epsilon^\ddagger} \quad (30)$$

where κ and $\epsilon^\ddagger$ represent the transmission coefficient and the classical activation energy, respectively. Substituting Eq. (30) into Eq. (17) and (22) yields

$$\sum_{ij} \sigma_{ij}(\epsilon - \epsilon_{ai} - \epsilon_{bj})(\epsilon - \epsilon_{ai} - \epsilon_{bj}) = \frac{\kappa h^2}{8\pi\mu} \cdot \frac{Q^{\text{int}}(\beta^*) e^{\beta^*(\epsilon - \epsilon^\ddagger)}}{\left\{ 2\pi \left[1 + \beta^{*2} \frac{\partial^2}{\partial\beta^{*2}} \log Q_{+}^{\text{int}}(\beta^*) \right] \right\}^{1/2}} \quad (31)$$

and

$$\bar{\sigma}_1(\epsilon) = \frac{\kappa h^2}{8\pi\mu} \cdot \frac{Q^{\text{int}}(\beta^*) e^{\beta^*(\epsilon - \epsilon^\ddagger)}}{W_E(\epsilon) \left\{ 2\pi \left[1 + \beta^{*2} \frac{\partial^2}{\partial\beta^{*2}} \log Q_{+}^{\text{int}}(\beta^*) \right] \right\}^{1/2}} \quad (32)$$

where β^* is determined by

$$\beta^{*-1} = \epsilon - \epsilon^\ddagger + \frac{\partial}{\partial\beta^*} \log Q_{+}^{\text{int}}(\beta^*). \quad (33)$$

To calculate $\bar{\sigma}_2(\epsilon)$ from Eq. (12), we have to evaluate b_2 , b_3 , and b_4 , which in this case are given by

$$b_2 = \frac{1}{2} \left[\frac{1}{\beta^{*2}} + \frac{\partial^2}{\partial\beta^{*2}} \log Q_{+}^{\text{int}}(\beta^*) \right] \quad (34-A)$$

$$b_3 = \frac{1}{3!} \left[-\frac{2}{\beta^{*3}} + \frac{\partial^3}{\partial\beta^{*3}} \log Q_{+}^{\text{int}}(\beta^*) \right] \quad (34-B)$$

and

$$b_4 = \frac{1}{4!} \left[\frac{3!}{\beta^{*4}} + \frac{\partial^4}{\partial\beta^{*4}} \log Q_{+}^{\text{int}}(\beta^*) \right] \quad (34-C)$$

Next we shall discuss the calculation of the energy density function $W_E(\epsilon)$. For this purpose, we introduce the relation [16, 14]

$$H(\epsilon) = \frac{1}{2\pi i} \int_{\gamma-i\infty}^{\gamma+i\infty} \frac{d\beta}{\beta} e^{\beta\epsilon} \quad (\gamma > 0) \quad (35)$$

into Eq. (21) to obtain

$$W_E(\epsilon) = \sum_{ij} (\epsilon - \epsilon_{ai} - \epsilon_{bj}) \frac{1}{2\pi i} \int_{\gamma-i\infty}^{\gamma+i\infty} \frac{d\beta}{\beta} e^{\beta(\epsilon - \epsilon_{ai} - \epsilon_{bj})}. \quad (36)$$

Using the definition of the partition function, Eq. (36) can be written as

$$W_E(\epsilon) = \frac{1}{2\pi i} \int_{\gamma-i\infty}^{\gamma+i\infty} \frac{d\beta}{\beta} \cdot \frac{\partial}{\partial \beta} [e^{\beta\epsilon} Q_{ab}^{\text{int}}(\beta)]. \quad (37)$$

To show applications of Eq. (37), we consider a harmonic oscillator. Classically, $Q^{\text{int}}(\beta)$ is given by

$$Q^{\text{int}}(\beta) = \frac{1}{\beta h\nu}. \quad (38)$$

Substituting Eq. (35) into Eq. (37) yields

$$W_E(\epsilon) = \frac{1}{2\pi i} \int_{\gamma-i\infty}^{\gamma+i\infty} \frac{d\beta}{\beta} \left(\frac{\epsilon}{\beta} - \frac{1}{\beta^2} \right) \frac{e^{\beta\epsilon}}{h\nu}. \quad (39)$$

By applying the Cauchy's residue theorem, we obtain,

$$W_E(\epsilon) = \epsilon^2/2h\nu. \quad (40)$$

Suppose we are concerned with the classical expression of the chemical reaction cross section for the reaction, $E + DC \rightarrow ED + C$. In this case, according to the absolute reaction rate theory, we have [11, 14]

$$Q_{ab}^{\text{int}}(\beta) = \frac{g}{\sigma} \cdot \frac{8\pi^2 I}{\beta h^2} \cdot \frac{1}{\beta h\nu} \quad (41)$$

and

$$Q_{\ddagger}^{\text{int}}(\beta) = \frac{g^{\ddagger}}{\sigma_{\ddagger}} \cdot \frac{8\pi^2 I_{\ddagger}}{\beta h^2} \cdot \frac{1}{\beta^3 h^3 \nu_b^2 \nu_s} \quad (42)$$

assuming the activated complex is linear. g (and $g^{\ddagger}$) and σ (and $\sigma_{\ddagger}$) represent the degeneracy factor and symmetry number, respectively.

From Eqs. (41) and (37), we obtain the energy density function,

$$W_E(\epsilon) = \frac{g}{\sigma} \cdot \frac{8\pi^2 I}{h^3 \nu} \cdot \frac{\epsilon^3}{3!} \quad (43)$$

Substitution of Eq. (42) into Eq. (32) gives

$$\bar{\sigma}_1(\epsilon) = \frac{\kappa g_{\ddagger}}{\sigma_{\ddagger}} \cdot \frac{\pi I_{\ddagger}}{\mu h^3 \nu_b^2 \nu_s \beta^{*4}} \cdot \frac{e^{\beta^*(\epsilon - \epsilon^{\ddagger})}}{(10\pi)^{1/2}} \cdot \frac{1}{W_E(\epsilon)} \quad (44)$$

where β^* is to be determined from Eq. (33), i.e., $\beta^* =$

$5(\epsilon - \epsilon^{\ddagger})^{-1}$. Combining Eqs. (43) and (44), we obtain

$$\bar{\sigma}_1(\epsilon) = \frac{\kappa g_{\ddagger} \sigma}{\sigma_{\ddagger} g} \cdot \frac{3\nu I_{\ddagger}}{4\pi I \mu \nu_b^2 \nu_s} \cdot \frac{e^5}{\sqrt{2\pi} 5^{4+1/2}} \cdot \frac{(\epsilon - \epsilon^{\ddagger})^4}{\epsilon^3} \quad (45)$$

which should be compared with the exact expression [14]

$$\bar{\sigma}(\epsilon) = \frac{\kappa g_{\ddagger} \sigma}{\sigma_{\ddagger} g} \cdot \frac{\nu I_{\ddagger}}{32\pi \mu I \nu_b^2 \nu_s} \cdot \frac{(\epsilon - \epsilon^{\ddagger})^4}{\epsilon^3}. \quad (46)$$

The difference between these two expressions is again simply due to the approximate Stirling relation. $4!/\sqrt{2\pi} (4+1)^{4+1/2} e^{-(4+1)} \sim 1$, as mentioned before. The second-order correction can be calculated easily from Eq. (12). In this case, it is $-1/60$, less than 2%, which indicates that in most cases, the first-order approximation of the steepest-descent method is sufficient in calculating the reaction cross section from a rate constant. From the above discussion, we can see that by using the method of steepest-descent, we can easily carry out the inverse Laplace transform of any rate constant to obtain the corresponding reaction cross section.

This work was supported by the National Science Foundation and the American Chemical Society's Petroleum Research Fund.

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