[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER, ROCHESTER 20, N. Y.]

Classical Unimolecular Rate Theory. Rotating Anharmonic Diatomic Molecules[1]

BY FRANK P. BUFF AND DAVID J. WILSON

RECEIVED JUNE 8, 1962

In theories of chemical kinetics employing the concept of a critical surface, it is usually assumed that the point of intersection of the critical surface and the reaction coördinate has a fixed value. The example of a rotating anharmonic diatomic molecule provides a case in which this assumption must be relaxed for the treatment of dissociation by means of unimolecular rate theory. Also, the region of phase space from which collisional deactivation may occur is found to be dependent on the nature of the collision process. The limitations of the random phase approximation are investigated. Explicit calculations are made for the high-pressure limit of the rate constant, and the effect of the centrifugal barrier leads to a somewhat larger pre-exponential factor than is obtained by ignoring rotational effects.

Among the various theories of gas reactions are several approaches which employ the concept of a critical surface in phase space which partitions the space into two parts, one corresponding to reactants, and one to products.[2,3] With few exceptions (for example, see references 4 and 5), these papers ignore interactions between rotations and vibrations, and they also assume that the intersection of the reaction coördinate and the critical surface is independent of temperature.

We shall concern ourselves with a classical approach to unimolecular reactions, and shall follow the methods of Slater[2a] and Thiele[2b] as they apply to the simplest of all possible unimolecular reactions, the dissociation of diatomic molecules. (Experimentally, of course, diatomic molecule dissociation can be studied only in the low-pressure limit.) The critical surface which immediately suggests itself is that corresponding to the top of the rotational barrier in the effective vibrational potential function. The results of this choice of critical surface will be investigated. However, this choice implies that the change in angular momentum of the diatomic molecule when it collides is negligible, which is not a particularly realistic assumption (but which is not significant in the high-pressure limit). We then briefly investigate a model in which large changes in the angular momentum of the molecule may occur on collision. The assumption of instantaneous collisions leads to certain internal inconsistencies, which we investigated. Lastly, the effect of rotations on the high-pressure limit of the dissociation is computed.

The Hamiltonian of a rotating diatomic molecule is

$$\begin{aligned} H &= (p_r^2/2\mu) + V_{\text{eff}}(r,p) \\ V_{\text{eff}} &= V(r) + (p^2/2\mu r^2) \end{aligned} \qquad (1)$$

where $V(r)$ is the potential energy of the bond, μ is the reduced mass, p_r is the momentum conjugate to r, and p is the total angular momentum of the diatomic molecule. If p remains essentially constant during a collision, a natural choice of the critical surface in phase space is $r = r_0(p^2)$, where r_0 is that value of r for which

$$\begin{aligned} (\partial V_{\text{eff}}/\partial r)_{\text{p}} &= 0 \\ (\partial^2 V_{\text{eff}}/\partial r^2)_{\text{p}} &\leqslant 0 \end{aligned} \qquad (2)$$

Consideration of a rotating molecule instead of a non-rotating one eliminates the arbitrariness in the specification of the reaction coördinate noted, for example, by Thiele.[6]

The critical coördinate is at the internuclear distance corresponding to the top of the rotational barrier; a molecule "deactivated" at a larger value of r will remain dissociated, since we here assume a negligible change in p^2.

Following Slater for the moment, we write

$$k = \frac{\int_0^{p^{\max}} \int_0^{r_0(p)} \int_{-\infty}^{\infty} \exp(-\omega s)\omega \exp(-\beta H)_p \mathrm{d}p_r \mathrm{d}r \mathrm{d}p}{\int_0^{p^{\max}} \int_0^{r_0(p)} \int_{-\infty}^{\infty} \exp(-\beta H)p \, \mathrm{d}p \, \mathrm{d}r \mathrm{d}p} \qquad (3)$$

where $\beta = (kT)^{-1}$, ω is the kinetic collision constant, and $r_0(p)$ is defined by eq. 2. $p^{\max}$ is the value of p which satisfies $(\partial V_{\text{eff}}/\partial r)_{\text{p}} = 0$, $(\partial^2 V_{\text{eff}}/\partial r^2)_{\text{p}} = 0$; this is the maximum value of the angular momentum for which bound states of the molecule can occur. $s(r,p_r,p)$ is the time required for a representative point starting initially at r, p_r, p to follow along its trajectory until it passes out through the critical surface. In this equation we have already performed the integrations over the angle variables and components of angular momentum.

If we now change variables to r, H and p, and integrate with respect to r, we find that

$$k = \frac{\int_0^{p^{\max}} \int_{H_{\text{dis}}(p)}^{\infty} [1 - \exp(-\omega s^*)] \exp(-\beta H)p \mathrm{d}H \mathrm{d}p}{\int_0^{p^{\max}} \int_{H_{\min}(p)}^{\infty} s(H,p) \exp(-\beta H)p \mathrm{d}H \mathrm{d}p} \qquad (4)$$

Here

$$s^* = 2 \int_{r_1(H,P)}^{r_0(p)} (\mu/p_r)\mathrm{d}r$$

where $r_1(H, p)$ is the classical turning point of the motion for unbound states. For bound states, $s = \oint (\mu/p_r)\mathrm{d}r$; for unbound states, $s = s^*$. $H_{\min}(p)$ is the minimum total energy possible when the total angular momentum is p; $H_{\text{dis}}(p)$ is the minimum total energy for which dissociation may occur, given that the total angular momentum is p.

Limiting values of k at the high-and-low-pressure limits can easily be extracted from eq. 4; the low-pressure limit is

---

[1] This work was supported by the National Science Foundation.

[2] (a) N. B. Slater, "Theory of Unimolecular Reactions," Cornell University Press, Ithaca, N. Y., 1959, and numerous papers by this author; (b) E. Thiele, *J. Chem. Phys.*, **36**, 1466 (1962).

[3] R. A. Marcus, *ibid.*, **20**, 359 (1952).

[4] H. Eyring, H. Gershinowitz and C. E. Sun, *ibid.*, **3**, 786 (1935).

[5] M. A. Eliason and J. O. Hirschfelder, *ibid.*, **30**, 1426 (1959).

[6] E. Thiele, Doctoral Dissertation, University of Rochester, 1961.

$$\lim_{\omega \to 0} k = \frac{\omega \int_0^{p^{\max}} \int_{H_{\mathrm{dis}}(p)}^{\infty} s^* \exp(-\beta H) p \mathrm{d}H \mathrm{d}p}{\int_0^{p^{\max}} \int_{H_{\min}(p)}^{\infty} s \exp(-\beta H) p \mathrm{d}H \mathrm{d}p} \tag{5}$$

as one would expect.

In our approach the effective temperature dependence of the intersection of the reaction coordinate with the critical surface has been concealed by making the critical surface a function of p, as well as r. This temperature dependence can most readily be displayed by calculating the average value of the reaction coördinate with respect to the molecules which react. The distribution function the instant after activation of the molecules which react is readily seen to be

$$(r,p,p_{\mathrm{r}},\beta)\mathrm{d}r\mathrm{d}p_{\mathrm{r}}\mathrm{d}p = \frac{\omega \exp\{-\omega s[p_{\mathrm{r}},r,p,r_0(p)]\}\, e^{-\beta H} p\mathrm{d}r\mathrm{d}p_{\mathrm{r}}\mathrm{d}p}{\int\int\int \omega \exp\{-\omega s[p_{\mathrm{r}},r,p,r_0(p)]\}\, e^{-\beta H} p\mathrm{d}r\mathrm{d}p_{\mathrm{r}}\mathrm{d}p} \tag{6}$$

in which the limits of integration are the same as those in eq. 4, so that

$$\langle r_0 \rangle = \int\int\int r_0(p) f(r,p,p_{\mathrm{r}},\beta)\mathrm{d}r\mathrm{d}p_{\mathrm{r}}\mathrm{d}p. \tag{7}$$

$\langle r_0 \rangle$ is obviously a function of temperature unless it is independent of p.

The above treatment of diatomic molecule dissociation assumes that the angular momentum of a molecule changes negligibly on collision even though the vibrational energy may change drastically. This led us to a critical surface which is a function of both r and p, in marked contrast to the usual type of critical surface, which is a function of coördinates but not momenta.[7]

We now relax this rather artificial restriction, and permit a strong collision mechanism[8] to operate with respect to angular momentum, as well as to vibrational energy. After an initial activating collision, the molecule will undergo at some later time a subsequent collision, which will, in general, change V_{eff}. The position of the representative point relative to the rotational barrier in this new V_{eff} will determine whether reaction or deactivation has occurred. We use the same Hamiltonian as before (eq. 1); we let p_1 be the total angular momentum *before* the deactivating collision, and p_2 be the total angular momentum of the molecule *after* the deactivating collision. A natural choice of critical surface is now $r = r_0(p_2)$, where $r_0(p_2)$ is the value of r for which $V(r) + (p_2)^2/2\mu r^2$ goes through a maximum. If the molecule is collisionally deactivated while $r < r_0(p_2)$, it will drop into a bound state; if it is deactivated when $r > r_0(p_2)$, the atoms will continue to fly apart.

We now set up the expression for the rate constant $k(p_2)$ for dissociation of molecules whose final angular momentum (after deactivation) is p_2 in exactly the same manner as before, except that the limits on the p_1 integration are now 0 and ∞, and the limits on the r-integration are 0 and $r_0(p_2)$. We then average this over a suitable distribution function for p_2 to get the observed rate constant.

In the same manner as before, we find that

$$k(p_2) = \frac{\int_0^{\infty} \int_{H_{\mathrm{dis}}(p_1)}^{\infty} p_1\{1 - \exp[-\omega s^*(p_1,H,p_2)]\} e^{-\beta H} \mathrm{d}p_1 \mathrm{d}H}{\int_0^{\infty} \int_{H_{\min}(p_1)}^{\infty} s e^{-\beta H} p_1 \mathrm{d}H \mathrm{d}p_1} \tag{8}$$

where $s = s^*$ in those regions in which s^* is defined; otherwise it is given by $\oint (\mu/p_{\mathrm{r}})\mathrm{d}r$, as before; in this region s is not a function of p_2. s^*, the time required for the representative point to pass in through the critical surface, reach the classical turning point and pass out through the critical surface, is evidently a function of p_2.

Let $g(\beta, p_2)$ be the normalized distribution function of p_2; then

$$k = \int_0^{\infty} g(\beta,p_2)k(p_2)\mathrm{d}p_2 \tag{9}$$

One possible reasonable surmise for $g(\beta, p_2)$ is to assume that $(p_2)^2/2\mu r_0(p_2)^2 = \beta^{-1}$, and use the resulting very sharply peaked distribution function as a rough approximation. Alternatively, one may assume that $(p_2{}^2/2\mu r_0(p_2)^2$ has a Boltzmann distribution. In either case, the procedure is equivalent to choosing a critical surface independent of p_2 but dependent on the temperature.

There are several points in connection with the employment of Slater's "new approach to unimolecular rate theory" which appear particularly clearly in the discussion of diatomic molecule dissociation. The first of these is the implicit assumption that the collisions are instantaneous compared to the time scale associated with the vibrational motions of the molecules.[9] The period of molecular vibration frequencies is of the order of 10^{-13} second, which is about one-third the time required for the average molecule at 1000°K. to travel a distance of one ångstrom, and of the order of one-tenth the time during which a colliding pair of particles will have appreciable van der Waals interactions. For complex molecules, whose activated states have lifetimes of the order of 10^{-9} to 10^{-11} second or so, the assumption of instantaneous collisions is probably a good one, even though the collisions are evidently by no means instantaneous on the molecular vibrations time scale. For simpler molecules, such as nitrous oxide, the assumption of instantaneous collisions would appear highly dubious.

If one accepts the assumption of instantaneous collisions and all the implications of this assumption, additional complications arise. For all unbound trajectories in phase space, collisions occurring when the representative point is sufficiently near the classical turning point will not be effective in deactivating the molecule. This is readily seen from Fig. 1, in which are drawn trajectories in the p_{r}–r phase plane. The outer trajectory is the one being traced out by the representative point; the inner trajectory is the trajectory of the most energetic bound state having the same angular momentum as the outer trajectory. If the molecule undergoes an impulsive collision while its representative point is on the arc ABC, it cannot possibly be deactivated to a bound state. For the

---

(7) See ref. 1, for example.

(8) F. P. Buff and D. J. Wilson, *J. Chem. Phys.*, **32**, 677 (1960).

(9) See J. C. Light, *J. Chem. Phys.*, **36**, 1016 (1962), for a treatment avoiding this assumption.

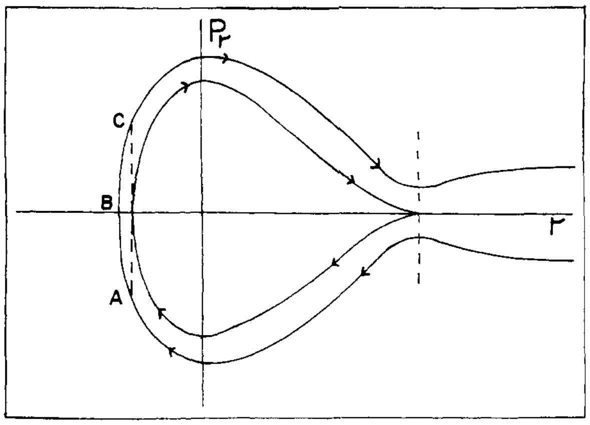

Fig. 1.—$p_r - r$ phase-plane diagram for "vertical" de-excitation.

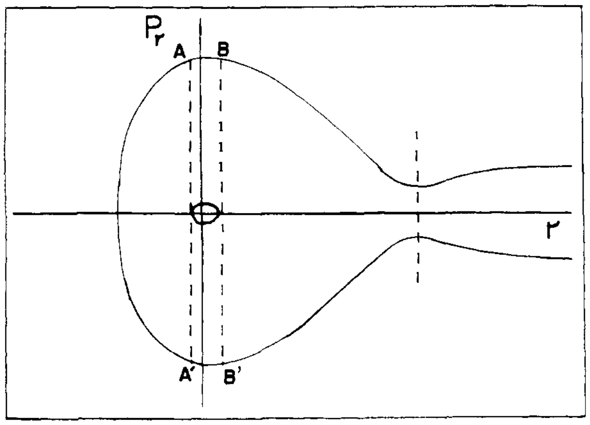

Fig. 2.—$p_r - r$ phase-plane diagram for "vertical" excitation.

sake of simplicity, we here assume that there is no change in the angular momentum of the molecule upon collision. One could obtain an upper bound to the magnitude of the discrepancy by simply denying the possibility of any collisional energy transfer occurring while the representative point is in this "non-vulnerable" region. These observations are explored in the Appendix for a single harmonic oscillator.

Another difficulty arises from the assumption of initial random phases the instant after collisional excitation occurs if we rigorously follow the implications of our instantaneous collision assumption. The nature of the difficulty is illustrated in Fig. 2, which is a phase plane diagram of the trajectories followed in the p_r–r plane before and after the exciting collision. It is generally assumed that collisional excitations to any and all points on the unbound trajectory to the left of the critical surface are all equally probable; that, within the restriction that the phase be such that the representative point lies on the "reactant side" of the critical surface, the initial phase is perfectly random. If our collisions are instantaneous, however, the initial phase will be restricted to correspond to only those points on the unbound trajectory between A and B and between A′ and B′.

In actual fact, the non-impulsive nature of the collisions in all probability makes the approximation of ignoring the last two difficulties a much better one than the above analysis would indicate. The finite durations of the collisions make a much larger portion of the trajectory accessible as initial conditions, and also should permit deactivation from portions of the trajectory from which instantaneous collisions could not induce deactivation.

Although the mapping of the pressure dependence of k requires machine calculations for general intramolecular potentials, the qualitative trend may be assessed by the evaluation of k_∞, which yields a much simpler result. In the high-pressure limit, the formalism reduces to that of transition state theory for the escape of a particle over a barrier arising from the superposition of a centrifugal potential on the anharmonic intramolecular potential. This calculation does not involve the ambiguities discussed above, which apply only under conditions of finite pressure. Thus[8]

$$k_\infty = 4\pi^2 \int\int\int |p_r/2\mu|\ \delta(r - r_0[p])e^{-\beta H}\mathrm{d}p_r\mathrm{d}r\mathrm{d}p^2/Q = \frac{4\pi^2}{Q}\int_0^\infty e^{-\beta p_r^2/2\mu}\,\mathrm{d}p_r^2/2\mu \int_0^{(p^{\max})^2} e^{-V_{\mathrm{eff}(\max)}}\,\mathrm{d}p^2 \quad (10)$$

where Q is the partition function for the molecule, and $\delta(r - r_0[p])$ is the Dirac delta function peaked at the maximum of the rotational barrier of V_{eff}. We note that at the barrier maximum the following relations hold

$$p^2/2\mu r^2 = r/2\,\mathrm{d}V/\mathrm{d}r$$

$$\frac{\mathrm{d}V}{\mathrm{d}R} + r/3\,\frac{\mathrm{d}^2V}{\mathrm{d}r^2} \leqslant 0 \quad (11)$$

The equality applies at the limiting (horizontal) point of inflection $r = r^+$, corresponding to maximum angular momentum.

It is convenient to change the integration variable from p to r, and for this purpose it is noted that

$$\left|\frac{\mathrm{d}p^2}{\mathrm{d}\mu r}\right| = -\,2r^2\,\frac{\mathrm{d}U(r)}{\mathrm{d}r}$$

$$U(r) = V(r) + r/2\,\frac{\mathrm{d}V}{\mathrm{d}r} \quad (12)$$

The desired expression for k_∞ may thus be written in the forms

$$k_\infty = \frac{8\pi^2\mu r^{+2}}{\beta Q}\int_1^\infty x^2\,\frac{\mathrm{d}U}{\mathrm{d}x}\,e^{-\beta U(x)}\,\mathrm{d}x;\ x = r/r^+ = \frac{8\pi^2\mu r^{+2}}{\beta^2 Q}\left\{1 - e^{-\beta U(r^+)} + 2\int_1^\infty [1 - e^{-\beta U(x)}] \times \mathrm{d}x\right\} \quad (13)$$

It will be noted that the final integrals are quite similar to those encountered for the second virial coefficient of gases, the latter being capable of interpretation in terms of the virial theorem or, for monotonic potentials,[10] in terms of thermally averaged scattering cross sections.

For the desired estimate of eq. 13, Q is adequately approximated by

$$Q \sim 8\pi^2\mu r_e^2 e^{\beta E_0}/\beta^2\nu$$

the harmonic approximation, provided that $\beta E_0 \gg 1$, where r_e is the minimum of $V(r)$, ν is the natural frequency for vibrations of small amplitude and E_0 is the activation energy; βE_0 will be taken to be

(10) J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, "Molecular Theory of Gases and Liquids," John Wiley and Sons, Inc., New York, N. Y., 1954.

40. The value of the remaining terms in k_∞ will not be qualitatively affected by the representation of $V(r)$ by a 12–6 Lennard-Jones potential, for which it is found that $U(r^+) = 0.8E_0$ and $r^+ = 1.23r_e$. The final result is

$$k_\infty \approx \nu e^{-\beta E_0} (r^+/r_e)^2 [2\beta U(r^+)]^{1/3} \Gamma(2/3) \approx 2.1 (\beta E_0)^{1/3} \nu e^{-\beta E_0} \quad (14)$$

The explicit use of the centrifugal potential thus tends to increase k_∞ over its familiar value $\nu e^{-\beta E_0}$ (see ref. 1, for example), which is obtained by taking the critical coördinate at infinity. This result may be of interest in view of the high values of the pre-exponential factors of some unimolecular rate constants at the high-pressure limit.

Appendix

It is the purpose of this appendix to illustrate that at finite pressures Slater's criterion of "interesting" states is inconsistent with the random phase assumption.[11] Here it is sufficient to consider the second order limiting rate constant k_0 for the simple case of a non-rotating harmonic oscillator. This system is characterized by the Hamiltonian

$$H = p^2/2\mu + \mu\omega^2 q^2/2 \quad (A1)$$

with interesting states defined by $q < q_0$ and $H \geqslant E_0 = \mu\omega^2 q_0^2/2$. The trajectory time s^* for these states is readily found to be

$$s^* = \frac{1}{\nu}\left(1 - \frac{\cos^{-1}\sqrt{E_0/H}}{\pi}\right) \quad (A2)$$

where ν is the natural frequency of the oscillator. The limiting rate constant may be exhibited in the alternative forms

$$k_0 = \nu\beta \int_{E_0}^{\infty} e^{-\beta H} s^*(H) \mathrm{d}H \quad (A3)$$

or

$$k_0 = \nu\beta \int_{J_0}^{\infty} \int_{q < q_0} e^{-\beta H} \mathrm{d}J \mathrm{d}\psi \quad (A4)$$

Equation A4 is written in terms of the angle variable ψ and action variable $J = H/\nu$. The inequality $q < q_0$, defining the interesting states, restricts the angle variable to

$$0 \leqslant \psi \leqslant 1 - \frac{\cos^{-1}\sqrt{J_0/J}}{\pi} \quad (A5)$$

so that upon substitution and partial integration

$$k_0 = e^{-\beta E_0} - \frac{e^{-\beta E_0}}{\pi} \int_0^{\infty} \frac{e^{-\beta E_0 u^2}}{1 + u^2} \mathrm{d}u \quad (A6)$$

The first term of eq. A6 constitutes the random phase assessment of k_0. The correction term possesses an upper bound given by

$$- k_0 + e^{-\beta E_0} = e^{-\beta E_0}/2\sqrt{\beta E_0 \pi} \quad (A7)$$

For representative cases of $\beta E_0 \approx 40$, the correction term decreases k_0 about 5%.

This example illustrates that the time scales for the collisional activation process and the subsequent dissociation require future clarification. Thus, vertical activation processes which would exclude states with $q < -q_0$ would double the correction in eq. A7.

---

[11] See N. B. Slater, *Proc. Roy. Soc. (London)*, **A194**, 112 (1948), p. 119, for comment on this point.

[Contribution from the Inorganic Chemistry Laboratory, University of Oxford, Oxford, Eng.]

The Recombination of Halogen Atoms

By Margaret I. Christie

Received June 27, 1962

Previous results on iodine atom recombination in the presence of rare gases have shown that the measured rate of recombination in a mixture containing a very low ratio of molecular iodine to rare gas is less than that calculated from the additive effect of molecular iodine and rare gas as third bodies. It is suggested that, under these conditions, the deactivation of the vibrationally excited iodine, formed as the initial product of the recombination, is the rate-determining step. The data for iodine and bromine atom recombination are discussed in relation to the various mechanisms of atomic recombination which have been proposed.

The recombination of atoms in the gas phase

$$\mathrm{X} + \mathrm{X} + \mathrm{M} = \mathrm{X}_2 + \mathrm{M}'$$

follows the kinetic law

$$\mathrm{d}(\mathrm{X}_2)/\mathrm{d}t = k_B(\mathrm{X})^2 = k_M \mathrm{M}(\mathrm{X})^2$$

In a mixture of gases

$$k_\mathrm{B} = \sum_M k_\mathrm{M} \mathrm{M}$$

where k_M is the third-order constant relating to species M. The function of the third body, M, is to remove some of the excess energy possessed by the two atoms and thus allow formation of the diatomic molecule.

The first extensive work on iodine and bromine atom recombination was that of Rabinowitch[1] who derived values of k_M for a variety of gases from photostationary measurements. The development of flash photolysis has made possible the direct measurement of the recombination of iodine[2–7] and bromine[4,8] atoms. Iodine values for k_M for some thirty gases have now been obtained; the values vary over a range of a thousand, helium

[1] E. Rabinowitch, *Trans. Faraday Soc.*, **33**, 283 (1937).

[2] K. E. Russell and J. Simons, *Proc. Roy. Soc. (London)*, **A217**, 271 (1953).

[3] M. I. Christie, A. J. Harrison, R. G. W. Norrish and G. Porter, *ibid.*, **A231**, 446 (1955).

[4] R. L. Strong, J. C. W. Chien, P. E. Graf and J. E. Willard, *J. Chem. Phys.*, **26**, 1287 (1957).

[5] D. L. Bunker and N. Davidson, *J. Am. Chem. Soc.*, **80**, 5085, 5091 (1958).

[6] R. Engleman and N. R. Davidson, *ibid.*, **82**, 4770 (1960).

[7] G. Porter and J. A. Smith, *Proc. Roy. Soc. (London)*, **A261**, 28 (1961).

[8] W. G. Givens and J. E. Willard, *J. Am. Chem. Soc.*, **81**, 4773 (1959).