Equal reaction rates for all recombination pathways

G. W. Wei, Saman Alavi, and R. F. Snider

Department of Chemistry, University of British Columbia, Vancouver V6T 1Z1, Canada
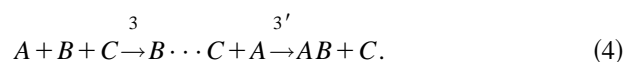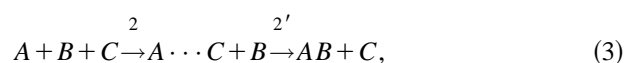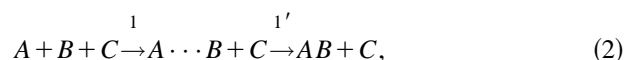
Formal collision theory indicates that the absolute termolecular recombination reaction rate can be expressed in a form associated either with direct or indirect mechanisms for the recombination. Moreover, the same exact rate constant can be calculated using either of the four mechanisms. These results are to be contrasted to the rate constants standardly calculated by approximate methods. © *1997 American Institute of Physics.* [S0021-9606(97)01104-5]

Collision pathways for the three molecules A, B and C to react to form the "dimer" AB, are standardly classified[1] as direct (type I) collisions symbolized by

$$A + B + C \xrightarrow{0} AB + C \tag{1}$$

and indirect (type II) collisions symbolized by

$$A + B + C \xrightarrow{1} A \cdots B + C \xrightarrow{1'} AB + C, \tag{2}$$

$$A + B + C \xrightarrow{2} A \cdots C + B \xrightarrow{2'} AB + C, \tag{3}$$

$$A + B + C \xrightarrow{3} B \cdots C + A \xrightarrow{3'} AB + C. \tag{4}$$

In the pure direct (type I) collision all three molecules A, B and C enter the three-body interaction region almost simultaneously, whereas in the indirect (type II) collisions a reaction intermediate or transient colliding pair (such as an orbiting resonance state) is established before the third molecule encounters the pair and the subsequent reaction leads to the formation of the bound dimer. The indirect collisions are standardly treated as a sequence of binary collisions. This classification of triple collisions according to types I and II has been regarded as rigorous[1] if the potentials involved are short ranged.

The chemically intuitive way of deciding the dominant mechanism of a reaction and the corresponding calculations that are performed, treat the intermediates as definite chemical entities with rovibrational, etc., states and consider the chemical reaction to proceed by *running over a pass on the potential energy surface along (or very close to) the lowest energy (classical or quantum wave packet) trajectory*. From this approximate point of view the rates for different pathways are not the same.

In this approach the usual view is that all pathways should contribute to the overall rate of the recombination process, i.e.,

$$k_r = k_0' + k_1' + k_2' + k_3'. \tag{5}$$

The primes on these rate constants emphasize their approximate nature. It is commonly believed that most three-body reactions proceed predominantly by type II and that the type I collision is relatively unimportant. Moreover it is usually assumed that the formation of the recombination product AB will likely be favored by only one of the collision mechanisms and the above sum is thus dominated by one term.

It is the purpose of the remainder of this communication to show that, according to the formal theory of microscopic three-body collision dynamics, if the rate constant for each pathway is calculated *exactly*, then all rate constants are equal and each separately describes the *complete* dynamics of recombination, that is

$$k_r = k_0 = k_1 = k_2 = k_3. \tag{6}$$

This clearly contradicts the usual chemical intuition that the rates for these processes are very different. The resolution of this dilemma is understood to be the recognition that the rate constants in Eqs. (5) and (6) are different. A further practical consequence of this distinction is that, if the approximate rate constants are added as in Eq. (5), there is a possibility that some of the transition probability may be doubly counted since the individual pathway calculations may monitor some of the same dynamics, namely that the same dynamics is only being described in a different manner.

The theoretical description of a three-body collision involves the three-body Liouville (super-)operators $\mathscr{L}$ and $\mathscr{L}_a$,

$$\mathscr{L} = \sum_{j=1}^{3} \mathscr{K}_j + \mathscr{V} = \mathscr{L}_0 + \mathscr{V}, \quad \mathscr{L}_a = \mathscr{L}_0 + \mathscr{V}_a, \tag{7}$$

where $\mathscr{K}_j$ is the kinetic energy superoperator of molecule j and $\mathscr{V}_a$ are rearrangement channel potential energy superoperators assuming pairwise additivity of the potentials. The particle pairs and collision channels are labeled according to Eqs. (2)–(4) with, for example, the pair AB being designated as 1 and the intrachannel potential designated as $\mathscr{V}_1 = \mathscr{V}_{AB}$ appropriate for when molecules A and B are interacting together and molecule C is free. The total potential energy superoperator $\mathscr{V}$ is assumed to be pairwise additive, so that

$$\mathscr{V} = \sum_{a=0}^{3} \mathscr{V}_a, \tag{8}$$

with $\mathscr{V}_0 = 0$ included for the noninteracting channel for notational symmetry.

In describing the kinetic theory of a gaseous system consisting of monomers of a particular species and their corresponding dimers, including the chemical reactions of dimer

recombination and decay, Snider and Lowry[2] express the rate constant for the recombination of molecules A and B to form the bound dimer AB using C as a third body in terms of the three-body transition superoperator $\mathscr{T}_{b0}(z)$, $(z \equiv \omega + i\epsilon)$. This is identical to the type I pathway since there is nothing in the description that determines whether all the molecules meet simultaneously, or not. By algebraic rearrangement, they found that $\mathscr{T}_{b0}(z)$ can be written as a sum of contributions, one from each of the three possible ''two-body'' intermediate states,

$$\mathscr{T}_{b0}(z) = \frac{1}{3} \sum_{a=1}^{3} \mathscr{T}_{ba}(z) \Omega_{\mathscr{L}_a, \mathscr{L}_0}(z). \tag{9}$$

Here the Møller superoperator[3,4] is given by

$$\Omega_{\mathscr{L}_a, \mathscr{L}_0}(z) = 1 + (\omega - \mathscr{L}_a + i\epsilon)^{-1}(\mathscr{L}_a - \mathscr{L}_0) \tag{10}$$

and the channel transition superoperators $\mathscr{T}_{b0}(z)$ and $\mathscr{T}_{ba}(z)$ are given in Lippmann–Schwinger form as

$$\mathscr{T}_{b0}(z) = \mathscr{V}^b \Omega_{\mathscr{L}, \mathscr{L}_0}(z)$$
$$= \mathscr{V}^b [1 + (\omega - \mathscr{L} + i\epsilon)^{-1}(\mathscr{L} - \mathscr{L}_0)], \tag{11}$$

and

$$\mathscr{T}_{ba}(z) = \mathscr{V}^b \Omega_{\mathscr{L}, \mathscr{L}_a}(z)$$
$$= \mathscr{V}^b [1 + (\omega - \mathscr{L} + i\epsilon)^{-1}(\mathscr{L} - \mathscr{L}_a)], \tag{12}$$

with the final state interaction potential superoperator given by

$$\mathscr{V}^b = \mathscr{V} - \mathscr{V}_b. \tag{13}$$

Obviously Eq. (9) can be rewritten as

$$\mathscr{T}_{b0}(z) = \frac{1}{3} \sum_{a=1}^{3} \mathscr{V}^b \Omega_{\mathscr{L}, \mathscr{L}_a}(z) \Omega_{\mathscr{L}_a, \mathscr{L}_0}(z). \tag{14}$$

This is an explicit relation between the termolecular reaction processes of types I and II. Equation (14) can be interpreted as stating that for given initial and final states of a termolecular reaction, the sum of the transition superoperators associated with type II collision processes (2–4) is three times that of the type I collision process.

The result of Snider and Lowry can actually be generalized and carried one step further. By using the definition of the Møller superoperator given in Eq. (10), it can be seen that for any general series of channels, here labelled α, β and γ for generality,

$$\Omega_{\mathscr{L}_\alpha, \mathscr{L}_\beta}(z) = 1 + (\omega - \mathscr{L}_\alpha + i\epsilon)^{-1}(\mathscr{L}_\alpha - \mathscr{L}_\beta)$$
$$= 1 + (\omega - \mathscr{L}_\alpha + i\epsilon)^{-1}(\mathscr{L}_\alpha - \mathscr{L}_\gamma)$$
$$+ (\omega - \mathscr{L}_\alpha + i\epsilon)^{-1}(\mathscr{L}_\gamma - \mathscr{L}_\beta)$$
$$= 1 + (\omega - \mathscr{L}_\alpha + i\epsilon)^{-1}(\mathscr{L}_\alpha - \mathscr{L}_\gamma)$$
$$+ (\omega - \mathscr{L}_\alpha + i\epsilon)^{-1}[(\omega - \mathscr{L}_\alpha + i\epsilon)$$
$$+ (\mathscr{L}_\alpha - \mathscr{L}_\gamma)](\omega - \mathscr{L}_\gamma + i\epsilon)^{-1}(\mathscr{L}_\gamma - \mathscr{L}_\beta)$$
$$= 1 + (\omega - \mathscr{L}_\alpha + i\epsilon)^{-1}(\mathscr{L}_\alpha - \mathscr{L}_\gamma)$$

$$+ (\omega - \mathscr{L}_\gamma + i\epsilon)^{-1}(\mathscr{L}_\gamma - \mathscr{L}_\beta)$$
$$+ (\omega - \mathscr{L}_\alpha + i\epsilon)^{-1}(\mathscr{L}_\alpha - \mathscr{L}_\gamma)$$
$$\times (\omega - \mathscr{L}_\gamma + i\epsilon)^{-1}(\mathscr{L}_\gamma - \mathscr{L}_\beta)$$
$$= [1 + (\omega - \mathscr{L}_\alpha + i\epsilon)^{-1}(\mathscr{L}_\alpha - \mathscr{L}_\gamma)]$$
$$\times [1 + (\omega - \mathscr{L}_\gamma + i\epsilon)^{-1}(\mathscr{L}_\gamma - \mathscr{L}_\beta)]$$
$$= \Omega_{\mathscr{L}_\alpha, \mathscr{L}_\gamma}(z) \Omega_{\mathscr{L}_\gamma, \mathscr{L}_\beta}(z). \tag{15}$$

A common frequency parameter ω for all Møller superoperators is required. Equation (15) can be recognized as Kato's chain rule[5] for Møller superoperators in spectral component form. This equation implies that, for the three-body collision schemes of (1–4),

$$\mathscr{T}_{b0}(z) = \mathscr{V}^b \Omega_{\mathscr{L}, \mathscr{L}_1}(z) \Omega_{\mathscr{L}_1, \mathscr{L}_0}(z)$$
$$= \mathscr{V}^b \Omega_{\mathscr{L}, \mathscr{L}_2}(z) \Omega_{\mathscr{L}_2, \mathscr{L}_0}(z)$$
$$= \mathscr{V}^b \Omega_{\mathscr{L}, \mathscr{L}_3}(z) \Omega_{\mathscr{L}_3, \mathscr{L}_0}(z), \tag{16}$$

or equivalently,

$$\mathscr{T}_{b0}(z) = \mathscr{T}_{ba} \Omega_{\mathscr{L}_a \mathscr{L}_0}(z) \quad \text{for } a = 1, 2 \text{ or } 3. \tag{17}$$

This is an extension of Eq. (14). Note that none of the Møller superoperators in steps 1, 2 or 3 nor in 1′, 2′ or 3′ are necessarily the same, that is $\Omega_{\mathscr{L}_1, \mathscr{L}_0} \neq \Omega_{\mathscr{L}_2, \mathscr{L}_0} \neq \Omega_{\mathscr{L}_3, \mathscr{L}_0}$ and $\Omega_{\mathscr{L}, \mathscr{L}_1} \neq \Omega_{\mathscr{L}, \mathscr{L}_2} \neq \Omega_{\mathscr{L}, \mathscr{L}_3}$, but the combined effect of Møller superoperators for successive collisions, $1 + 1′ = 2 + 2′ = 3 + 3′$ are the same, as indicated by Eq. (16). It will be shown below that this implies an equality of reaction rate constants for all the mechanisms described by Eqs. (1–4).

As discussed by Snider and Lowry,[2] the energy averaged absolute termolecular reaction rate constant k_a for each of the reaction pathways can be obtained from the transition and Møller superoperators. For the mechanism shown by Eq. (1), this rate constant is given by

$$k_0 = (q_A q_B q_C)^{-1} \Lambda^{-3}(m_A + m_B + m_C) \Lambda^3(m_A) \Lambda^3$$
$$\times (m_B) \Lambda^3(m_C) \sum_{rs} W^0_{0r \to bs} \exp(-E_{0r}/kT), \tag{18}$$

where the q_j's are the internal state partition functions of each of the initial molecules and the thermal de Broglie wavelength for a particle of mass m is $\Lambda(m)$. $W^0_{0r \to bs}$ is the transition probability of going from the original three free molecules A, B and C, labeled as ''rearrangement'' channel 0 in relative motion state r, to the final dimer product AB with its (third-body) collision partner C, labeled here as rearrangement channel b (for ''bound'' state) in relative motion state s, via the direct pathway 0 described by Eq. (1). E_{0r} is the kinetic energy of relative motion for the molecules in state r. The transition probability has been shown to be given by

$$W^0_{0r \to bs} = (i\hbar)^{-1} \text{Tr}_{\text{rel}} P_{bs} \mathscr{T}_{b0} P_{0r}, \tag{19}$$

where for example, P_{bs} is the projector onto state s of the three particle rearrangement channel b. The trace is over all states of relative motion with the presumption that the center of mass motion of the three molecules has been removed from discussion. It should also be remarked, that in the present work, the molecules A, B and C are treated as distinct species, whereas the discussion in Ref. 2 is restricted to identical species, with the consequence that there is, in that work, an extra factor of 3 multiplying Eq. (18) to account for the possibility that any of the three pairs of molecules could end up being bound.

For each one of the other three pathways, the rate constant is

$$k_a = (q_A q_B q_C)^{-1} \Lambda^3(\mu_a^t) \Lambda^3(\mu_a)$$
$$\times \sum_{rs} W_{0r \to bs}^a \exp(-E_{0r}/kT). \tag{20}$$

Here μ_a^t is the reduced mass of the interacting pair in pathway a of the reaction [for example, $\mu_1^t = m_A m_B / (m_A + m_B)$ for the pathway of Eq. (2), $a = 1$], and μ_a is the reduced mass of the lone fragment with respect to the center of mass of the interacting pair [$\mu_1 = m_C(m_A + m_B)/(m_A + m_B + m_C)$ for Eq. (2)]. In each case the transition probability can be written as

$$W_{0r \to bs}^a = (i\hbar)^{-1} \text{Tr}_{\text{rel}} P_{bs} \mathscr{T}_{ba} \Omega_{\mathscr{L}_a, \mathscr{L}_0} P_{0r}, \tag{21}$$

where a labels the channel associated with the relative motion and internal states for the transient pair and free fragment during the intermediate step in the mechanism. Equation (17) implies the equality of transition probabilities, $W_{0r \to bs}^0 = W_{0r \to bs}^a$ The prefactors of Eqs. (18) and (20) are also equal, which follows from the identity,

$$\Lambda^3(m_A) \Lambda^3(m_B) \Lambda^3(m_C) = \Lambda^3(m_A + m_B + m_C)$$
$$\times \Lambda^3(\mu_a^t) \Lambda^3(\mu_a). \tag{22}$$

In this way the equality of the exact rate constants for the different pathways is established, Eq. (6).

The effect of the Møller superoperator on the state of a pair of non-interacting molecules is to replace the "free" state with an interacting state having the same energy. Denoting the (relative motion) state of the transient pair (plus third particle) by l in rearrangement channel a, produced from initial state r of rearrangement channel 0, the transition probability associated with mechanism a can be written as

$$W_{0r \to bs}^a = (i\hbar)^{-1} \text{Tr}_{\text{rel}} P_{bs} \mathscr{T}_{ba} P_{al}, \tag{23}$$

with $P_{al} \equiv \Omega_{\mathscr{L}_a, \mathscr{L}_0} P_{0r}$ being the projector onto the transient state al. As a consequence, the mechanism a rate constant can be expressed as (a sum over l of) a product of an equilibrium constant for the transient state al, here exemplified for Eq. (2) [$a = 1$],

$$K_1^l \equiv (q_A q_B)^{-1} \Lambda^3(\mu_1^t) e^{-E_{1l}/kT}, \tag{24}$$

and a "bimolecular" rate constant

$$k_{1l \to bs} = q_C^{-1} \Lambda^3(\mu_1)(i\hbar)^{-1} \text{Tr}_{\text{rel}} P_{bs} \mathscr{T}_{b1} P_{1l}, \tag{25}$$

namely

$$k_1 = \sum_{l,s} k_{1l \to bs} K_1^l. \tag{26}$$

Note that $1l$ refers to a *single* intermediate state.

As the authors see it, the distinction between Eqs. (5) and (6) is related to how many l states are included in the sum in Eq. (26). While the exact rate constant involves *all* intermediate l states, the usual method of estimating reaction rate constants, and the usual chemical rationalization of how the molecules react, is based on picking out those intermediate states with the largest rate constant and using only those states. This leads to the difference between k_a and k_a'. Thus in practical calculations and in experimental situations, a reaction process is usually interpreted in terms of a minimum energy (classical) trajectory (or quantum wave packet motion near the classical minimum energy trajectory) along the potential energy surface of a particular pathway.[6,7] The choice of pathway for practical calculations is dictated by that which provides the lowest energy barrier for the reaction and for recombination reactions, to those intermediate (orbiting and/or resonance) states that have the longest life. In carrying out such a procedure, not all states in any particular pathway are included, so it is not apparent from the calculations that are usually done that there is an equivalence of pathways. But this does not imply that the sum of the rates from all intermediate states for a second pathway does not give the same total rate constant as for the first pathway. Nor does it exclude the possibility of some double counting of transition probability if one adds the minimum energy rates calculated for different pathways.

An illustration of the standard approach to the explicit calculation of the rate constants of different type II pathways is the calculation for the hydrogen recombination reaction,

$$H + H + M \to H_2 + M \tag{27}$$

with $M = H_2$, He, or Ar, carried out by Pack, Snow and Smith.[8] They generally classify type II recombination reactions of A atoms as energy transfer (ET) mechanisms,

$$A + A \rightleftharpoons A \cdots A,$$
$$A \cdots A + C \to A_2 + C, \tag{28}$$

or bond-complex (BC) mechanisms,

$$A + C \rightleftharpoons A \cdots C,$$
$$A \cdots C + A \to A_2 + C, \tag{29}$$

and calculate approximate rates of recombination for each of these separate mechanisms, based on selecting out only the longest lived transient states. They neither obtain the same rate constants, nor the same temperature dependence, for the rate constants for the ET and BC pathways.

Detailed information about the presence of reactive intermediates can be obtained by molecular beam scattering.[9,10] While the above arguments are stated for energy averaged absolute rate constants, the equivalence of recombination pathways is also valid for state-to-state absolute rate constants since Eq. (16) really is for individual quantum states. But consistent with the remarks in previous para-

graphs, what will be experimentally observed, or more correctly, how the experiments are most easily interpreted, will be in terms of the longest-lived states (narrowest resonances)[6,7] and so whichever pathway allows the longest-lived intermediates will be the one that is most useful for the description of the recombination reaction. That does not imply that the whole collision process cannot be described via a different pathway, only that this alternative is likely not as efficient computationally or conceptually, in that its dynamical motion will probably be much more elaborate.

Two constraints on the above arguments are immediately obvious, each of which could significantly influence the applicability of the above formal results to the interpretation of experimentally measured rate constants. First of all, it has been assumed that the potential is pairwise additive. Surely this is false for chemically reacting systems. But it is not clear that this should change the above formal arguments for any particular type II pathway, since all that is required is separating the potential into a pair potential for determining the transient pair state, plus the remainder. If the remainder contains nonpairwise additive terms, does it really matter? The second constraint is the fact that what is described is an *isolated* three-body collision. The standard chemical argument of a collision complex is that it has to live long enough for energy to be transferred into a mode that allows the reaction to take place. If energy transfer to other molecules in the system (via collisions with the transient without deactivation to form a bound state) are important for this reorganization of the complex, the reaction is *not* just a three-body collision and the present reaction schemes (1–4) are insufficient for a true description of the kinetics of the reaction. If such is the case, then the results of this communication may not be directly applicable to the interpretation of experimental results.

Except for the constraints discussed in the preceeding paragraph, the collision properties discussed here are independent of the detailed form of the potential surface as long as it is short ranged. As mentioned above, the transition superoperator relation (16) follows immediately from Kato's chain rule for the Møller superoperator. Kato's chain rule is a rigorous relation that has stimulated much interesting research in atomic, molecular and nuclear physics by suggesting certain physical divisions and approximations based on exact mathematical relations.[11] The arguments of this work can also be applied to three-body collisions in these other fields.

[1] F. T. Smith, in *Kinetic Processes in Gases and Plasmas*, edited by A. R. Hochstim (Academic, New York, 1969).
[2] R. F. Snider and J. T. Lowry, J. Chem. Phys. **61**, 2330 (1974).
[3] J. M. Jauch, B. Misra, and A. G. Gibson, Helv. Phys. Acta. **41**, 513 (1968).
[4] R. F. Snider and B. C. Sanctuary, J. Chem. Phys. **55**, 1555 (1971).
[5] T. Kato, *Perturbation Theory for Linear Operators* (Springer, New York, 1966).
[6] B. Kendrick and R. T. Pack, Chem. Phys. Lett. **235**, 291 (1995).
[7] W. H. Miller, J. Phys. Chem. **99**, 12387 (1995).
[8] R. T. Pack, R. L. Snow, and W. D. Smith, J. Chem. Phys. **56**, 926 (1972).
[9] U. Buck, in *Atomic and Molecular Beam Methods*, edited by G. Scoles, D. Bassi, U. Buck, and D. Lainé (Oxford University Press, New York, 1988), Vol. I.
[10] Y. T. Lee, in *Atomic and Molecular Beam Methods*, edited by G. Scoles, D. Bassi, U. Buck, and D. Lainé (Oxford University Press, New York, 1988), Vol. I.
[11] Gy. Bencze and C. Chandler, Phys. Rev. Lett. **72**, 3925 (1994); Phys. Rev. C **45**, 532 (1992); Gy. Bencze, P. Doleschall, C. Chandler, A. G. Gibson, and D. Walliser, *ibid.* **43**, 992 (1991).