Study of Atomic Recombination Over a Wide Pressure Range[1]

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Abstract: The mechanism of atomic recombination over a wide pressure range is investigated. A generalized formal expression for recombination of two atoms in the presence of *n* "chaperon" molecules is obtained and applied to the special case of iodine-atom recombination in argon at 300°K. The information on the recombination mechanism was deduced from the simplified version of the generalized expression, earlier 3-D trajectory calculations, and the available experimental data. It was found that if the total argon concentration is of the order of, or less than, 0.02 mol/l., which corresponds to about 0.5 atm, the recombination proceeds *via* three-body interactions. If the argon concentration is of the order of 0.2 mol/l., *i.e.*, about 5 atm, four-body interactions contribute to combination. When the argon concentration is further increased to about 1.0 mol/l., *i.e.*, about 25 atm, five-, and higher, body interactions appear to contribute to recombination. At argon concentrations of 1.0 mol/l. or below, the simplified version of the generalized expression accounts for some 95% of the overall recombination process. If the argon concentration is 10.0 mol/l. which corresponds to about 350 atm, the gas density is such that the time of interaction of two iodine atoms is of the order of the time between collisions. In this case, argon exhibits an appreciable deviation from ideal behavior and the atomic recombination is almost pseudo-second-order reaction, its rate being approximately independent of [Ar]. This finding is supported by the available experimental data.

Ever since the first paper on flash photolysis was published, atomic recombination reactions in the gas phase have been investigated in great detail.[2]

More recently, atomic recombination over a wide temperature range was studied.[3-7] In order to explain these experimental data, various theoretical models[8,9] were proposed. Classical 3-D trajectory calculations[10-16] were successful in predicting the absolute value and temperature dependence of atomic recombination rate constants.

The theoretical models and trajectory calculations usually assumed that the recombination in the gas phase proceeds either *via* the energy transfer (ET) mechanism

$$X + X \rightleftharpoons X_2^* \qquad (1)$$

$$X_2^* + M \longrightarrow X_2 + M \qquad (2)$$

or *via* the radical-molecule complex (RMC) mechanism.

$$X + M \rightleftharpoons XM \qquad (3)$$

$$XM + X \longrightarrow X_2 + M \qquad (4)$$

Here X_2^* is an unbound quasidimer, as defined by Kim and Ross,[17] XM is either a weakly bound dimer or a quasidimer intermediate, and M is a third body, usually an inert gas, present in concentrations much larger than [X] and $[X_2]$.

Reactions 1-4 involve an assumption that the atomic recombination proceeds *via* three-body interactions only. In the past, this assumption was usually accepted *ad hoc* and was not tested in any way. The aim of the present work is to (a) estimate the pressure range at which such an assumption breaks down, (b) explain the nature of this breakdown, and (c) compare the conclusions, obtained in (a) and (b), with the available experimental data.

Results

Recombination of atoms at high densities and pressures of the "chaperon" gas may be written in the following general form

$$2X + nM \longrightarrow X_2 + nM \qquad (5)$$

where *n* is the number of M atoms or molecules which interact with two X atoms in an $(n + 2)$-body collision, yielding X_2 product. For reaction 5, the generalized rate constant, defined by $d[X_2]/dt = k_r^{\text{obsd}}[X]^2[M]$, is

$$k_r^{\text{obsd}} = \left\{K_0\left(\sum_{d=1}^{d=n} k_{0n}[M]^{d-1}\right) + \sum_{f=1}^{f=n}\sum_{g=1}^{g=0.5f+y}\left(\prod_{j=1}^{j=p}K_j\right)\left(\prod_{i=0}^{i=q}K_i\right)k_{pq}[M]^{g-1}\right\} \Bigg/ \left\{1 + \sum_{h=1}^{h=n}\left(\prod_{l=1}^{l=h}K_l\right)[M]^h\right\}^2 \qquad (6)$$

In eq 6, subscripts for all equilibrium constants, *K*, refer to the total number of M in the colliding complex. Thus, the equilibrium constant for XM complex, eq 3, is K_1, while K_0 refers to the equilibrium constant for eq 1. The first subscript of the rate constant, *k*, refers to the total number of M in the first partner, while the second subscript refers to the total number of M in the second partner. Thus defined, the rate constant for eq 4 is k_{10}. In order to avoid confusion between ET and RMC mechanisms, the rate constants which describe RMC mechanisms have the first subscript always larger than the second, while the first subscripts in ET mechanism rate constants are always zero. For example, the rate constant for eq 2 is k_{01}.

Equation 6 is subject to the following conditions: (1) $p + q = n$; (2) $p \geq q \geq 0$; (3) y is 0.5 if f is odd, and unity if f is even; (4) d, f, n, p, and q are positive integers, except that q can be zero. Equation 6 involves the assumption that $K_0[X] \ll 1$. This assumption is nearly always fulfilled in all experiments. Thus, in all flash photolysis experiments on iodine atom recombination, $[I] \simeq 10^{-5}$ mol/l. and K_0 is of the order[14] of 10^{-1} l./mol. The first and the second terms in the numerator of eq 6 provide the generalized expression for the ET mechanism and the RMC mechanism, respectively. Reactions $XM_m + oM \rightleftharpoons XM_{m+o}$ are omitted in this formal approach because recombination involving these equilibria can be included in recombination *via* $XM_n + M \rightleftharpoons XM_{n+1}$ equilibrium, provided K_{n+1} is properly calculated.

For the special case of recombination *via* three-body interactions only, *i.e.*, eq 1-4, eq 6 reduces to[1]

$$k_r^{\text{obsd}} = (K_0k_{01} + K_1k_{10})(1 + K_1[M])^{-2} \qquad (7)$$

If the contribution from four-body interactions is to be included, the following reactions have to be considered in the reaction scheme:

ET term

$$X_2^* + 2M \xrightarrow{k_{02}} X_2 + 2M \tag{8}$$

RMC terms

$$XM + M \overset{K_2}{\rightleftharpoons} XM_2 \tag{9}$$

$$XM_2 + X \xrightarrow{k_{20}} X_2 + 2M \tag{10}$$

$$2XM \xrightarrow{k_{11}} X_2 + 2M \tag{11}$$

Then, the recombination involves only three- or four-body interactions and eq 6 reduces to

$$k_r^{\text{obsd}} = \frac{K_0(k_{01} + k_{02}[M]) + k_{10}K_1 + K_1(k_{11}K_1 + k_{20}K_2)[M]}{(1 + K_1[M] + K_1K_2[M]^2)^2} \tag{12}$$

Similarly, if five-body interactions are to be included, the corresponding equations are

ET term

$$X_2^* + 3M \xrightarrow{k_{03}} X_2 + 3M \tag{13}$$

RMC terms

$$XM_2 + M \overset{K_3}{\rightleftharpoons} XM_3 \tag{14}$$

$$XM_3 + X \xrightarrow{k_{30}} X_2 + 3M \tag{15}$$

$$XM_2 + XM \xrightarrow{k_{21}} X_2 + 3M \tag{16}$$

$$k_r^{\text{obsd}} = \{K_0(k_{01} + k_{02}[M] + k_{03}[M]^2) + k_{10}K_1 + K_1(k_{11}K_1 + k_{20}K_2)[M] + K_1K_2(k_{21}K_1 + k_{30}K_3)[M]^2\}/(1 + K_1[M] + K_1K_2[M]^2 + K_1K_2K_3[M]^3)^2 \tag{17}$$

In order to assess the magnitude of four-, and higher, body interactions in atomic recombination at high pressures of M, we plotted in Figure 1 the $k_r^{\text{obsd}}[M]$ *vs.* [M] (eq 7) for the special case of $2I + Ar$ (or Xe) $\rightarrow I_2 + Ar$ (or Xe) reactions. In this figure, pressures, *i.e.*, the upper abscissa, were calculated from concentrations using the ideal gas law. The values of K_0, k_{01}, K_1, and k_{10} were obtained previously using classical trajectory calculations by Wong and Burns.[14] Two independent variables were investigated in Figure 1: the depth of the L-J interaction potential, ϵ_∞^{IM}, and absolute temperature.

It can be deduced from Figure 1 that all curves display negative second derivative. Thus, if $\epsilon_\infty^{IAr} = 0.6$ kcal/mol and $T = 300°K$, the linear relationship between k_r^{obsd} and [Ar] is violated already at about 0.2 mol/l., which corresponds to about 5 atm. This, on first sight, is a remarkably low pressure. However, $\epsilon_\infty^{IAr} = 0.6$ kcal/mol is probably a realistic depth for the I-Ar intermolecular potential. Thus, recently Lee,[18] using the cross-molecular beam technique, found that the intermolecular potential for I-Ne dimer, ϵ_∞^{INe}, is equal to 0.33 kcal/mol. If usual combination rules are applied to this value of ϵ_∞^{INe}, it is found that ϵ_∞^{IAr} is 0.61 kcal/mol. Furthermore, when $\epsilon_\infty^{IAr} = 0.6$ kcal/mol is used in trajectory calculations,[14] it yields the absolute value of the recombination rate constant and its temperature dependence in fair agreement with experiment. If larger values of ϵ_∞^{IAr} are used, the deviation from linearity (Figure 1) occurs at lower concentrations. Thus, for $\epsilon_\infty^{IAr} = 1.3$ kcal/mol at 300°K, $k_r^{\text{obsd}}[Ar]$ is virtually independent of [Ar] at approximately 0.7 mol/l. When calculations were extended to even higher concentrations, the curves displayed a negative first derivative.

Deviation from linearity is much less pronounced at higher temperatures. For example, the plot of $k_r^{\text{obsd}}[Ar]$ *vs.* [Ar] for $\epsilon_\infty^{IAr} = 0.6$ kcal/mol at 1500°K is nearly linear up to 1 mol/l. and is still increasing with concentration at 1.8 mol/l.

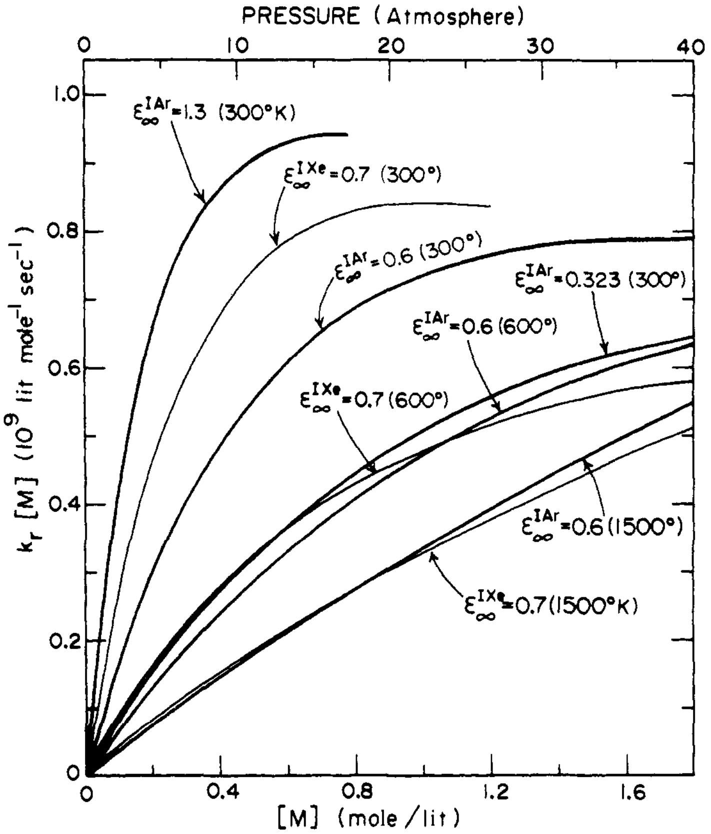

Figure 1. Second-order recombination rate constant, $k_r[M]$ *vs.* [M] = [Ar] or [Xe] for various I-M interactions and at several temperatures.

All the above results (Figure 1) can be explained in terms of shifts in the equilibrium in eq 3 and in terms of eq 7. At high concentrations of M the assumption that $K_1[M] \ll 1$ breaks down, and therefore the denominator in eq 7 is larger than unity. The equilibrium in eq 3 is shifted to the right, whereby the concentration of free iodine atoms, and therefore the overall three-body recombination rate (eqs 2 plus 4), is depressed. Deviation from linearity (Figure 1) occurs at a relatively low pressure because, as shown previously by Wong and Burns,[14] as well as by earlier workers, the IM and I_2^* complexes are relatively large, can be formed at impact parameters as large as 8 Å, and produce I_2 molecules which, being in highly excited vibrational-rotational states near the dissociation limit, have large internuclear distances. If the temperature is increased, the equilibrium constant K_1 is decreased, and the equilibrium in eq 3 is shifted to the left, which increases the concentration of free atoms and yields curves with only a slight negative second derivative (Figure 1). Results involving Xe are consistent with those involving Ar and with the above explanations (Figure 1).

Curvatures displayed in plots on Figure 1 signify that [IM] may not be negligible compared to [I]. Therefore, deviation from linearity (Figure 1) implies that four, *i.e.*, reactions 10 and 11, and possibly higher, body interactions contribute to the overall recombination reaction and play a more significant role at higher concentrations and pressures of M, at lower temperatures, and for stronger XM interactions.

The main difficulty with eq 6, 12, and 17 is lack of knowledge of relevant equilibrium and rate constants. However, it is possible to obtain useful information on $(n + 2)$ body recombination in the following limiting cases.

Case I. Low-Pressure Limit, Which Implies That Only Three-Body Recombination (eq 1-4) is Possible. Since this case was studied previously both experimentally and theoretically, it will not be considered further here.

Case II. Predominance of One Specific Interaction in the Recombination Process. This approximation was considered earlier[19] for a special case of $2I + NO \rightarrow I_2 + NO$ reaction, because NOI is a relatively stable intermediate. In this case only eq 3, 4, 9, and 11 had to be included, and eq 10 could be safely omitted. Therefore, a simplified version of eq 12, in which it was assumed that $K_0 = K_2 = 0$, was used. Experimental curves, similar to those shown in Figure 1, demonstrated[19] a negative second derivative.

Case III. Moderate Total Pressure and Nonspecific Interactions. This case is important if the interaction between the recombining atom and chaperon is of the weak van der Waals type. Such a situation arises if the chaperon is an inert gas. For this case, reasonable four- or five-body equilibrium and rate constants may be estimated using an appropriate physical model and knowledge[14] of k_{10}, k_{01}, K_0, and K_1, which is obtained from trajectory calculation studies. In order to construct such a physical model it was necessary to invoke the following three assumptions.

(1) Since the interaction between X and M is of the van der Waals type, all bonds between X and M in an XM_n complex are of equal strength. Therefore, we accept a simple assumption that all equilibrium constants for the XM_n complexes are equal, provided that M in the complex is the nearest neighbor of X. If M is not the nearest neighbor to X, we assume that it does not contribute to the recombination reaction. Since a reasonable number of nearest neighbors is six, this assumption requires that $K_1 \simeq K_2 \simeq K_3 \simeq K_4 \simeq K_5$ but $K_{>5} = 0$.

(2) In any "bimolecular" collision, such as eq 10 or 11, an M atom, interacting loosely with an I atom, is just as likely to promote recombination as to hinder it. This assumption means that all bimolecular recombination rate constants, such as k_{10}, k_{11}, k_{20}, etc., are approximately equal.

(3) The generalized ET recombination mechanism, *i.e.*, reactions 8, 13, etc., involves a collision of an unbound I_2^* orbiting pair, with I-I distance small compared to I-M distance at the onset of the collision. On the other hand, if the initial separation between I and one of the M is small compared to I-I distance, such a collision is included in our RMC mechanism. Therefore, if the concentration of M is large, M will be in the vicinity of I, and the generalized RMC mechanism would contribute to the reaction, while the generalized ET mechanism will be unimportant. On the other hand, at moderately low pressures, the generalized ET mechanism (eq 8, 13, etc.), which involves tetra- and pentamolecular reactions, would make but a small contribution to recombination. For these reasons, and because in the present calculations $[I] \ll [M]$, we assume that $k_{02} \simeq k_{03} \simeq k_{04} \ldots \simeq k_{0n} \simeq 0$.

Although the above assumptions may provide useful order of magnitude information, their advantages and limitations can be determined quantitatively only by comparison with experiments and $(n + 2)$-body trajectory calculations.

Case IV. High Pressure Limit. In this case, the recombination rate is approximately independent of the concentration of the third body, because M is always present in the neighborhood of recombining pairs. This condition is approximately satisfied if the total pressure of the third body is so high that the time between collisions, t_c, is approximately equal to, or is smaller than, the time of interaction, t_i. In case IV, eq 6 should be modified because the recombination rate should be proportional to the "effective," rather than actual, concentration of M. Its solution may be approximated by considering diffusion of recombining atoms in a dense fluid of constant density.

Table I. Contribution of Various Iodine Recombination Mechanisms (%) in Argon at Various Argon Concentrations at 300°K

[Ar], mol/l.	3-body RMC + ET	4-body RMC mechanisms	5-, 6-, and 7-body RMC mechanisms	Unaccounted remainder
0.02	98	2	0.02	0
0.2	78	13	3	6
1.0	31	26	38	5

Comparison with Experiment

Recently, recombination rate constants for I atoms in inert and simple gases were measured between 0.5 and 1000 atm.[20,21] These measurements indicate that, in general $k_r^{\mathrm{obsd}}[M]$, eq 6, is proportional to [M] below about 100 atm for most simple third bodies, but displays negative curvature between about 100 and 1000 atm for all third bodies, except He. These experimental results suggest that deviations from linearity (Figure 1) are indeed due to four, and higher, body recombination processes. In Table I, the approximations discussed above (Case III) are applied to eq 6 to estimate per cent contribution of various mechanisms. As previously, $\epsilon_\infty^{\mathrm{IAr}} = 0.6$ kcal/mol, which yields[14] $K_1 \simeq 0.60$ l./mol, is used. The experimentally observable[20,21] linear dependence of $k_r^{\mathrm{obsd}}[\mathrm{Ar}]$ *vs.* [Ar] is assumed to hold in these calculations. If the argon pressure is about 0.5 atm, which corresponds to [Ar] = 0.02 mol/l., the concentration commonly used in flash photolysis experiments for k_r determination, the recombination proceeds exclusively (98%) *via* three-body mechanism. This approximates well our Case I. If [Ar] = 0.2 mol/l., *i.e.*, about 5 atm, the three-body recombination is still the predominant mechanism. However, the four-body recombination, *via* eq 10 and 11, is significant. Interestingly, at such concentrations, approximations of case III account for 94% of recombination processes. If [Ar] = 1 mol/l. the five-, six-, and seven-body recombination become important, while only about a third of the product is formed *via* three-body processes (Table I). About 16% of recombination appear to proceed *via* the five-body RMC mechanism. Despite major changes in the reaction mechanism, which occur as [M] is increased, the approximations used in case III still account for 95% of recombination reactions for the case of [Ar] = 1 mol/l.

In order to estimate the argon concentration at which case IV adequately represents the physical situation, it is possible to use data in Table III of ref 14 which indicate that the average half-life of two colliding iodine atoms, *i.e.*, I_2^*, is 2.33×10^{-12} sec at 300°K. Thus, the rate constant k_{-1} for the I_2^* decomposition, *i.e.*, the reciprocal time of interactions of two iodine atoms, is of the order of 4×10^{11} sec^{-1}. On the other hand, the reciprocal time between collisions I_2^* and Ar is of the order of $k_2^{\mathrm{eq}} = (3.76 \times 10^{10})[\mathrm{Ar}]$ sec^{-1}. If the time of interaction is approximately equal to the time of collision, then $k_{-1} \simeq k_2^{\mathrm{eq}}[\mathrm{Ar}]$. Thus, this calculation predicts that the recombination reaction should become approximately pseudo-second order if argon concentration is of the order of 10 mol/l. which corresponds to about 350 atm. This finding agrees well with the experiments.[20,21]

Since in case IV the recombination is a pseudo-second-order reaction, the reverse process, *i.e.*, the dissociation of diatomic molecules at very high pressures, should be a pseudo-first-order process. This conclusion is supported by results of Troe and Wagner,[22,23] who have shown that a transition to the first-order region takes place in shock wave dissociation of I_2 at 1060°K and total pressure of diluent gas above 100 atm. Previous authors[22,23] interpreted their experimental finding by suggesting that, at high pressures, the shock wave dissociation of iodine proceeds unimolecularly. Furthermore, they drew a parallel between unimolecular reaction of polyatomic molecules at high pressure limit and I_2 shock wave dissociation at 100 atm. This interpretation differs from our interpretation.

It may be of some interest to compare present calculations with those of Hippler, *et al.*[20,21] Hippler, *et al.*,[20] calculated that for IAr dimer, $K_1 \simeq 0.3$ l./mol. More recently, Hippler, *et al.*,[21] reported that $K_1 = 0.13$ l./mol. On the other hand, we calculated by the trajectory method that $K_1 = 0.6$ l./mol, if quasidimers are included, and 0.26 l./mol if the dimers are assumed to consist of bound and metastable species only.[14] However, Hippler, *et al.*, deduced their values of K_1 entirely from the curvature of $k_r^{\text{obsd}}[\text{Ar}]$ *vs.* [Ar] plots. In their experiments, the curvature becomes apparent only above 100 atm which corresponds to densities close to that of a liquid. In this pressure region, according to our estimates, many-body interactions dominate the recombination processes, while pure three-body recombination processes play a relatively minor role. Therefore, the agreement in K_1 value between our work[14] and that of Hippler, *et al.*,[20,21] appears to be fortuitous. In other words, it appears that K_1, as calculated by Hippler, *et al.*,[20,21] has little to do with the reaction $I + M \rightleftharpoons IM$ it supposes to describe. It should be noted that Hippler *et al.*,[20] included only one type of four-body collision, *i.e.*, eq 11, and neglected recombination *via* eq 10.

Hippler, *et al.*,[20] have suggested that for iodine recombination in argon, a change in the reaction order from 3 to 2.6, and then again to 3, at argon pressures at about 1 atm is due to a change from ET mechanism to RMC mechanism, which, they suggest, occurs when $k_1 \simeq k_{01}[\text{Ar}]$, where k_{-1} is the reverse of reaction 1. This explanation is not supported in our studies because, according to trajectory calculations,[14] k_1 is of the order of reciprocal time of interaction of two unbound iodine atoms *i.e.*, 4×10^{11} sec^{-1} On the other hand, k_{01} is 1.4×10^9 l./mol^{-1} sec^{-1}, as shown earlier.[14] This implies that the approximate equality $k_1 \simeq k_{01}$ [Ar] would be satisfied only at densities some eight times higher than density of liquid argon at 77°K! Reasons for a change in order were discussed previously.[14]

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