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Author
Mahan, Bruce H.

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University of California

Ernest O. Lawrence
Radiation Laboratory

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Bruce H. Mahan

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A Mechanism for Ion-Neutral Association Reactions

Bruce H. Mahan[*]

Inorganic Materials Division of the Lawrence Radiation
Laboratory and Department of Chemistry, University of
California, Berkeley, California

Abstract

The formation of diatomic molecular ions
from atomic ions in the presence of their parent
atoms can take place by a three body association
reaction that involves resonant charge transfer.
An approximate rate constant for this process
can be formulated simply, and calculated rates
are in good agreement with experimental data.
This mechanism should be an important loss process
for ions moving rapidly in a low temperature gas.

[*]Alfred P. Sloan Foundation Fellow.

In investigations[1,2,3] of the diffusion and mobility of atomic ions in their parent vapor, fairly rapid formation of diatomic molecular ions has been observed. The association reaction is second order with respect to neutral atoms, and can be represented, for example, by

$$He^+ + He + He \longrightarrow He_2^+ + He.$$
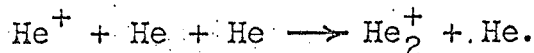
By analogy with other recombinations, it is natural to think of this three body process as one in which one member of an unbound ion-atom collision complex collides with the third particle, and thereby loses enough kinetic energy of relative motion to form a bound molecular ion. At least one[4] estimate of the recombination rate has been made on this basis. However, in cases where an ion collides with a parent atom, there is another mechanism for molecule formation, possibly of more importance. The recombination rate associated with this mechanism can be estimated readily.

Consider an ion (particle 1) that undergoes a grazing collision with an identical neutral, particle 2. At some distance from both, there is another neutral of arbitrary identity, particle 3. Particles 1 and 2 may undergo a resonant charge transfer that leaves particle 2 charged. Because the principal contribution to the charge transfer cross section comes from collisions with relatively large impact parameters, in most cases the kinetic energy of particle 2 will be changed only slightly in the charge transfer process. If after the charge transfer the mutual potential energy of particles 2 and 3

is negative and larger in magnitude than their relative kinetic energy, the pair is a bound diatomic molecular ion. Since in the idealized process the velocities of all particles are relatively unaltered, the association can be said to occur by means of a potential energy transfer rather than by the more familiar approximation of an impulsive kinetic energy exchange.

To compute the rate of association by this mechanism, we assume that the final potential between particles 2 and 3 is of the ion-induced dipole type. Furthermore, we assume this potential does not act until after the charge transfer process is over. This is surely a simplification, for during the resonant charge transfer the charge oscillates between particles 1 and 2, and in a rough approximation may be thought of as located midway between them. If the distance between particles 1 and 2 is large, and the charge transfer collision of relatively short duration, then the idealization of having the charge appear suddenly at particle 2 may not be too serious an approximation. The large cross sections for resonant charge transfer, and relatively high primary ion velocities such as those found in mass spectrometer sources favor the assumptions made here.

Particles 2 and 3 will be bound if after the charge transfer

$$\frac{1}{2} \mu g^2 \leq \frac{\alpha e^2}{2r^4} ,$$

(1)

where μ is the reduced mass, g is the relative speed, r is the separation of particles 2 and 3, α is the polarizability of particle 3, and e is the electron charge. Equation (1) allows us to define for each value of g a maximum critical radius r_c given by

$$r_c = \left(\frac{\alpha e^2}{\mu g^2}\right)^{1/4} \qquad (2).$$

If the separation of particles 2 and 3 is less than r_c, a bound molecular ion is formed as a result of the charge transfer. The third order association rate is given by the rate of charge transfer collisions times the chance that the third particle lies within a sphere of radius r_c centered on particle 2. The third order rate constant k' is accordingly

$$k' = k_{CT} \frac{4\pi}{3} \int_0^\infty r_c^3(g) \, f(g) \, dg \qquad (3)$$

where k_{CT} is the rate constant for charge transfer collisions, and $f(g)$ is the distribution function for relative speeds, which under the assumptions used here is the Maxwell-Boltzmann function.

It has been assumed that the charge transfer between particles 1 and 2 is of the resonant type, but this cannot strictly be true if particles 2 and 3 are close enough to interact. The error introduced by this assumption is rather small, however. Most of the contribution to the rate will come from configurations in which particles 2 and 3 eventually interact with an ion-induced dipole energy of the order of kT, and this energy can be taken as roughly equal to the resonance

defect of the charge transfer. Demkov[5] has shown that if the resonance defect is small compared to $(2 mI)^{1/2} v$, where m is the atomic mass, I is the ionization energy, and v is the ion-neutral relative velocity, then the charge transfer probability does not differ markedly from that of the case of exact resonance. This condition is met for typical values of the ionization energy.

With these limitations in mind, we can evaluate Eq. (3). We have

$$\frac{k'}{k_{CT}} = \frac{16\pi^2}{3}\left(\frac{\mu}{2\pi kT}\right)^{3/2}\left(\frac{\alpha e^2}{\mu}\right)^{3/4}\int_0^\infty g^{1/2}e^{-\mu g^2/2kT}\,dg$$

$$k' = \frac{4}{3}\pi^{1/2}2^{1/4}\,\Gamma\left(\frac{3}{4}\right)\,k_{CT}\left(\frac{\alpha e^2}{kT}\right)^{3/4} \qquad (4)$$

There are rather few data with which calculations based on Eq. (4) can be compared. Careful measurements of the three body association rates in pure helium and neon have been made by Beaty and Patterson,[1] and by Phelps and Brown[6] for helium. Estimates of the rates of reactions that are evidently

$$Ar^+ + Ar + He \longrightarrow ArHe^+ + Ar$$
$$A^+ + Ar + Ne \longrightarrow ArNe^+ + Ar$$
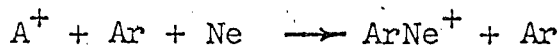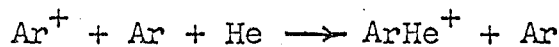
have been made by Oskam.[7] From these reactants the homonuclear ions may be formed also, but this must occur through a kinetic energy transfer mechanism rather than the charge transfer process discussed here. The kinetic energy transfer process is less likely to be important in situations where there is

a large mass discrepancy among the particles. Table 1 contains
a comparison of the calculated and observed association rates.
The polarizabilities were taken from Pitzer,[8] and the charge
transfer rate constants were evaluated by multiplying the
cross sections tabulated by Dalgarno[9] by the root-mean-square
relative speed. The relatively good agreement between the
calculations and the observations is encouraging, but consid-
erably more data are required before the true importance of
the charge transfer mechanism can be ascertained. The fact
that the calculated rate constants do not substantially exceed
the observed values suggests that this mechanism cannot be the
only contributor to the association rate.

Since the foregoing formulation relates the recombination
rate to the charge transfer cross section, it appears super-
ficially similar to the arguments recently put forth by
Beaty and Patterson.[10] The details and results of the two
treatments are quite different, however, since Beaty and
Patterson are not concerned with the details of the deacti-
vation process, and in effect choose what we have called r_c
always to be equal to $(2Q/\pi)^{1/2}$, where Q is the charge transfer
cross section. This choice leads to calculated recombination
rates that are smaller than found experimentally, and to a
temperature dependence different from what we have found.

Recently, Niles and Robertson[11] showed that the rate
constant for the termolecular formation of He_2^+ is inversely
proportional to temperature in the range from 77° to 443°K,

and that this dependence can be explained in terms of a simple collisional recombination mechanism in which charge transfer effects and any specific velocity dependence of collision cross sections are ignored. In their derivation, Niles and Robertson assume that the important collisions that dissociate molecule-ions are those in which the full dissociation energy is transferred in one event. This assumption is ultimately responsible for the derived inverse temperature dependence of the recombination rate constant. The "strong collision" mechanism is distinctly different from our point of view that collisions that produce weakly bound molecule-ions contribute significantly to the recombination rate, and that correspondingly, a "step ladder" mechanism for the dissociation process is important.

Equation (4) shows that the recombination rate constant for the charge transfer mechanism is proportional to $T^{-3/4}$ times some temperature factor associated with the charge transfer rate constant. The latter involves at least a factor of $T^{1/2}$ that corresponds to the velocity of relative motion. For relatively high ion energies, the charge transfer cross section depends on the logarithm of the relative velocity, and thus this factor should be rather insensitive to temperature. However, for thermal ions, the polarization correction[12] to the charge transfer cross section can be appreciable, and the effective charge transfer cross section should be written as

$$Q = \frac{\pi b_c^2}{2} [1 + (\alpha e^2/2Eb_c^4)]$$

Here b_c is the (virtually temperature independent) impact

parameter that corresponds to collisions in which the charge transfer probability is one half, and E is the energy of relative motion of the ion and neutral. At low temperatures, the charge transfer cross section may eventually become inversely proportional to temperature. Thus the temperature dependence of the recombination rate constant may range from $T^{-5/4}$ at low temperatures, to $T^{-1/4}$ at high temperatures. In addition, redissociation of weakly bound molecule-ions, which we have not considered, can introduce additional inverse temperature dependence.

As a guide to future experiments in this area, it should be noted that at high field strengths, the ion velocity will be large, and association via the kinetic energy transfer mechanism will be rather improbable, since large amounts of kinetic energy must be transferred in the ion-third particle collision. The charge transfer mechanism is most apt to be important in these circumstances, for the resonant charge transfer process replaces a fast ion with a slow ion. Since the charge transfer cross section falls only logarithmically with increasing velocity, the product of ion velocity and transfer cross section will remain large even at moderately high field strengths.

References

1. E. C. Beaty and P. Patterson, Proc. Sixth. Int. Conf. on Ionization Phenomena in Gases, Paris, 1963, S.E.R.M.A., Paris, 1964, Vol. I, p. 311.

2. J. A. Hornbeck, Phys. Rev. 84, 615 (1951).

3. J. S. Dahler, J. L. Franklin, M. S. B. Munson, and F. H. Field, J. Chem. Phys. 36, 3332 (1962).

4. D. R. Bates, Phys. Rev. 77, 718 (1950).

5. Y. N. Demkov, in Atomic Collision Processes, Ed. M. R. C. McDowell, North-Holland, Amsterdam, 1964, p. 831.

6. A. V. Phelps and S. C. Brown, Phys. Rev. 86, 102 (1952).

7. H. J. Oskam, Philips. Res. Repts. 13, 401 (1958).

8. K. S. Pitzer, Quantum Chemistry, Prentice-Hall, New York, 1953, p. 339.

9. A. Dalgarno, Phil. Trans. Roy. Soc. (London), A250, 426 (1958).

10. E. C. Beaty and P. L. Patterson, Phys. Rev. 137, A347 (1965).

11. F. E. Niles and W. W. Robinson, J. Chem. Phys. 42, 3277 (1965).

12. J. W. Sheldon, J. Appl. Phys. 34, 444 (1963).

Table I

Third Order Association Rate Constants

$(cm^6/molecule^2 sec)$

	Experimental	Ref.	Calculation
$He^+ + He + He$	10.8×10^{-32}	1	7.7×10^{-32}
	6.3×10^{-32}	6	
$Ne^+ + Ne + Ne$	5.8×10^{-32}	1	6.2×10^{-32}
$Ar^+ + Ar + He$	7.5×10^{-32}	7	4.9×10^{-32}[a]
$Ar^+ + Ar + Ne$	25×10^{-32}	7	8.3×10^{-32}[a]

a. Calculated assuming heteronuclear ion is formed.