We define the *second-order* rate constants, for a particular M

$$k_{\text{app}} = \mathrm{d}[\mathrm{I}]^{-1}{}_{\text{app}}/\mathrm{d}t \text{ and } k = \mathrm{d}[\mathrm{I}]^{-1}/\mathrm{d}t \qquad (9)$$

The fractional corrections calculated for these will be the same as for the customary third order constant. Differentiating eq. 8 with $[\mathrm{I}_2]$ approximately constant leads to

$$k_{\text{app}} = (1 + 4y[\mathrm{I}_2]/[\mathrm{I}])k + 2([\mathrm{I}_2]/[\mathrm{I}]^2)\mathrm{d}y/\mathrm{d}t \qquad (10)$$

For convenience this is rewritten

$$k_{\text{app}} = k(1 + c_1 + c_2) \qquad (11)$$

where $c_1 = 4y[\mathrm{I}_2]/[\mathrm{I}]$ and $c_2 = (2[\mathrm{I}_2]/k[\mathrm{I}]^2)\mathrm{d}y/\mathrm{d}t$.

To evaluate the c's, a series of dimensionless parameters is introduced: $C\Delta T = \alpha\phi\Delta H$; $\Delta T/T = h\alpha\phi$; $h = \Delta H/CT$. ϕ is $[\mathrm{I}_2]/[\mathrm{M}]$; α, initial degree of dissociation; $\Delta H \cong 60$ kcal./mole; and C is a heat capacity of M between C_v and C_p. y is then given by $-2gh\alpha\phi(Dt)^{1/2}/r$. The extent of recombination is described by a variable $\beta = [\mathrm{I}]_0/[\mathrm{I}]$, where $[\mathrm{I}]_0$ is the atom concentration just after the flash. Time can then be replaced by $t = (\beta - 1)/[\mathrm{I}]_0\, k$. Substitution of these quantities into the definition of c_1 results in

$$c_1 = (8gh\alpha\phi[\mathrm{I}_2]/r[\mathrm{I}])(D_1\{\beta - 1\}/Pk[\mathrm{I}]_0)^{1/2} \qquad (12)$$

wherein D has been made pressure-dependent, D_1 being the heat diffusivity at 1 atm. Use of $\alpha[\mathrm{I}_2] = (1/2)[\mathrm{I}]_0$ in eq. 12 reduces it to

$$c_1 = -(4gh\beta\phi/r)(D_1\{\beta - 1\}/Pk[\mathrm{I}]_0)^{1/2} \qquad (13)$$

The estimation of c_2 starts from

$$\mathrm{d}y/\mathrm{d}t = -gh\alpha\phi(Dt)^{1/2}/rt$$

$$c_2 = -2[\mathrm{I}_2]gh\alpha\phi(Dt)^{1/2}/rkt[\mathrm{I}]^2 \qquad (14)$$

If t is written in terms of β and α eliminated as before, and the result compared with eq. 13, it is revealed that

$$c_2 = (c_1/4)\beta/(\beta - 1) \qquad (15)$$

This allows the correction eq. 11 to be written in the form

$$k_{\text{app}}/k = 1 - [\beta(5\beta - 4)/4(\beta - 1)^{1/2}]x$$

where

$$x = (4gh\phi/r)(D_1/Pk[\mathrm{I}]_0)^{1/2} \qquad (16)$$

In eq. 16, x is a number characterizing the experimental conditions, and the β bracket is a universal time factor applicable to all experiments. x was evaluated for our argon measurements, with the values $C = 4$ cal./mole, $h = 50$, $g = 2.5$ and $r = 2.5$ cm., and found to be between 5×10^{-2} and 3×10^{-3}, with the higher value only rarely attained. Our β runs from 1.1 to, at most, 3, with the rate constant obtained from the slope of the second-order plot at $\beta = 1.1$; the value of the β bracket ranges from 1.3 to about 6 in this interval. Appreciable deviation from linearity seldom was found and would not be expected on the basis of the above treatment. Under our experimental conditions the error in the measured rate constant, due to thermal effects, is probably less than 1%.

PASADENA, CALIF.

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On the Interpretation of Halogen Atom Recombination Rates[1]

BY DON L. BUNKER AND NORMAN DAVIDSON[2]

RECEIVED MARCH 15, 1958

A theory for the rate of recombination of halogen atoms, X, in the presence of various third bodies, M, is developed. The theory assumes the formation of an equilibrium concentration of MX complexes. It is furthermore assumed that the recombination reaction, $\mathrm{MX} + \mathrm{X} \rightarrow \mathrm{M} + \mathrm{X}_2$, takes place only when MX is in a bound state, with internal kinetic energy less than the binding energy. For the case of chemically inert M's, a Lennard-Jones potential between M and X is used and an *a priori* statistical calculation gives good agreement with the measured rate constants and their temperature coefficients. The theory does not explain the cases, M = H_2, D_2 and He, however. In the special case that the third body is I_2 (in I atom recombination) the intermediate complex is chemically bound and its thermodynamic properties may be estimated from the recombination rate. The present data give, for the reaction $\mathrm{I}_2 + \mathrm{I} \rightarrow \mathrm{I}_3$, $\Delta H^0 = -5.3$ kcal., $\Delta S^0 = -20$ e.u.

There is now available a considerable amount of kinetic data pertaining to recombination of halogen atoms in the gas phase. Christie, Harrison, Norrish and Porter,[3] Strong, Chien, Graf and Willard[4] and the present authors[5] have all recently studied various aspects of the recombination rate of iodine atoms in the presence of argon and a few other added gases. Russell and Simons[6] have compiled a great deal of useful data relating the third-body efficiencies of various gases in this reaction. The reverse dissociation process had been studied above 1000°K. in the shock tube for iodine[7] and for bromine.[8,9] Room temperature measurements of the recombination rate of bromine atoms have been reported.[4]

As a result of these investigations, several general features of the recombination reactions have emerged.

(a) The termolecular rate constants have a small negative temperature coefficient

(b) There is a wide variation in effectiveness among the various gases which may be added as

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[1] This work was supported by the Office of Naval Research. Presented in part before the Division of Physical and Inorganic Chemistry, National Meeting of the American Chemical Society, New York, Sept. 11, 1957.

[2] To whom inquiries concerning this paper should be addressed.

[3] M. I. Christie, A. J. Harrison, R. G. W. Norrish and G. Porter, *Proc. Roy. Soc.* (*London*), **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. Bunker and N. Davidson, THIS JOURNAL, **80**, 5085 (1958).

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

[7] D. Britton, N. Davidson, W. Gehman and G. Schott, *J. Chem. Phys.*, **25**, 804 (1956).

[8] D. Britton and N. Davidson, *ibid.*, **25**, 810 (1956).

[9] H. B. Palmer and D. F. Hornig, *ibid.*, **26**, 98 (1957).

third bodies (which we call M). As pointed out by Russell and Simons, the relative efficiency of various third bodies correlates roughly with their boiling points, indicating that the strength of the intermolecular force between M and I or I_2 is important.

(c) As a corollary to (b), I_2 itself is a remarkably efficient recombination catalyst for I atoms.

(d) Our data[5] for argon, butane and iodine as third bodies support the generalization that the magnitude of the negative temperature coefficient is greater for those third bodies which are most efficient at low temperatures. This point is controversial since it is not supported by the earlier results of Russell and Simons.[6]

As is well known, discussion of a triple collision, such as the reaction

$$\mathrm{I} + \mathrm{I} + \mathrm{M} \longrightarrow \mathrm{I}_2 + \mathrm{M} \qquad (1)$$

is conveniently divided into a sequence of two bimolecular steps. In the present instance, there are two such sequences possible

$$\mathrm{I} + \mathrm{I} \rightleftarrows \mathrm{I}_2^* \qquad (2)$$

$$\mathrm{I}_2^* + \mathrm{M} \longrightarrow \mathrm{I}_2 + \mathrm{M} \qquad (3)$$

or

$$\mathrm{M} + \mathrm{I} \rightleftarrows \mathrm{MI} \qquad (4)$$

$$\mathrm{MI} + \mathrm{I} \longrightarrow \mathrm{M} + \mathrm{I}_2 \qquad (5)$$

Item (b) above was first revealed by the early photostationary state measurements.[10] Rabinowitch[11] then argued that the large variation in catalytic efficiency with M could not be explained by the reaction sequence 2 and 3, but would be expected if (4) and (5) were the main reaction path. This view has been supported by later authors.[12,13]

The remarkable efficiency of I_2 as M is reasonably attributed to the formation of a chemical compound, I_3, as the intermediate MI.[3,14] Some quantitative aspects of this interpretation will be discussed later in this paper.

For the case of more inert molecules as M, for example the noble gases or aliphatic hydrocarbons, the interaction between M and I involves van der Waals forces only. The principal purpose of the present paper is to present a quantitative theory of the reaction sequence 4 and 5 which explains most (but not all) of the experimental data.

A Theory of the MX Interaction.—Let X represent the atoms that are recombining, for example iodine atoms. Complexes MX in bound states must be themselves formed by a termolecular process, which can be written as

$$\mathrm{M} + \mathrm{X} \rightleftarrows \mathrm{MX}^* \qquad (4a)$$

$$\mathrm{MX}^* + \mathrm{M} \rightleftarrows \mathrm{MX} + \mathrm{M} \qquad (4b)$$

MX* is an energized MX molecule with kinetic energy greater than the potential energy of interaction between M and X. The recombination involves the additional reaction 5. In the presence of a large excess of M (but possibly not in a gas consisting largely of X atoms), reactions 4a and 4b will be fast compared to (5), provided that the binding energy of MX is small. MX will then be in equilibrium with M and X according to (4), undisturbed by (5). Stated more simply, MX is formed by the termolecular processes, $\mathrm{M} + \mathrm{X} + \mathrm{M} \rightarrow \mathrm{MX} + \mathrm{M}$, whereas over-all recombination proceeds by $\mathrm{M} + \mathrm{X} + \mathrm{X} \rightarrow \mathrm{X}_2 + \mathrm{M}$. If $(\mathrm{M}) >> (\mathrm{X})$, the former process is faster. We can therefore use statistical mechanics to calculate the concentration of MX.

We now write

$$k_{\mathrm{R}} = P_5 Z_5 K_4 \qquad (6)$$

k_4 is the equilibrium constant for reaction 4, Z_5 is a collision number for reaction 5, P_5 is a steric factor which we take (for X = iodine atoms) as 1 for M = I_2 and 1/2 for all other M, and k_{R} is the over-all recombination rate constant.

M may be a complex molecule but we treat it as a spherically symmetric atom. Let r be the MX distance and $\epsilon(r)$ their potential of interaction. This is taken as the Lennard-Jones potential

$$\epsilon(r) = 4\epsilon_0[(\sigma/r)^{12} - (\sigma/r)^6] \qquad (7)$$

ϵ_0 is the depth of the potential at its minimum and σ the internuclear separation, other than infinity, at which the potential is zero.

The phase space for the diatomic molecule MX is bounded in configuration space in a spherically symmetric region, $\sigma < r < \sigma_1$. The internal kinetic energy (vibration plus rotation) of MX is restricted to be between zero and $-\epsilon(r)$. This is the fundamental and novel (and essentially *ad hoc*) assumption in our treatment. *The recombination takes place by reaction of X atoms with those molecules MX which are in bound states, i.e., states of internal kinetic energy plus potential energy less than zero.* It will be seen later that σ_1 can be replaced by infinity.

If the complex XM has more than a very few bound states, the classical phase integral is a good approximation to its internal partition function Q_{int}. That this is nearly always the case for our purposes may be shown in several ways, one of which[15] consists of counting the number of cells of volume h^3 which may be fitted into the phase space which corresponds to the bound molecule. The approximate number of quantum states is

$$0.056\ (\sigma^2\mu\epsilon_0/k)^{1/2} \qquad (8)$$

where k is Boltzmann's constant. To find the potential parameters for XM we assume that the properties of the halogen atoms are adequately described by the values obtained from viscosity or virial coefficient measurements for the corresponding inert gases (*i.e.*, $\epsilon_0{}^{\mathrm{I}} = \epsilon^{\mathrm{Xe}}$, $\sigma^{\mathrm{Br}} = \sigma^{\mathrm{Kr}}$, etc.), and use the usual mixture rules

$$\epsilon_0{}^{\mathrm{XM}} = (\epsilon_0{}^{\mathrm{X}}\ \epsilon_0{}^{\mathrm{M}})^{1/2}$$

$$\sigma^{\mathrm{XM}} = (\sigma^{\mathrm{X}} + \sigma^{\mathrm{M}})/2 \qquad (9)$$

This scheme of interaction potentials will be used throughout this paper; other approximate methods of estimating the Lennard-Jones parameters of XM lead to substantially the same results. The system we have chosen leads us to expect 12-15 energy levels, for example, for the complex IA; those cases where there are so few levels that the use

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[10] E. Rabinowitch and W. C. Wood, *Trans. Faraday Soc.*, **32**, 907 (1936); *J. Chem. Phys.*, **4**, 497 (1936).

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

[12] R. Marshall and N. Davidson, *J. Chem. Phys.*, **21**, 659 (1953).

[13] M. I. Christie, R. G. W. Norrish and G. Porter, *Proc. Roy. Soc. (London)*, **A216**, 152 (1953).

[14] M. I. Christie, R. G. W. Norrish and G. Porter, *Disc. Faraday Soc.*, No. 17, 107 (1954).

[15] K. S. Pitzer, "Quantum Chemistry," Prentice-Hall, Inc., New York, N. Y., 1953, p. 340 ff.

of the phase integral is not warranted will be treated separately.

We formulate the phase integral in polar coordinates, immediately integrating the two sets of angles.

$$Q_{\text{int}} = (4\pi)^2 h^{-3} \int_{\sigma}^{\sigma_1} e^{-\epsilon/kT} \left[\int_{0}^{(-2\mu\epsilon)^{1/2}} e^{-p^2/2\mu kT}\, p^2 \mathrm{d}p \right] r^2 \mathrm{d}r \quad (10)$$

$$= (4\pi)^2 h^{-3} (2\mu kT)^{3/2} \int_{\sigma}^{\sigma_1} e^{-\epsilon/kT} [(\pi^{1/2}/4)\, \mathrm{erf}(-\epsilon/kT)^{1/2} - (1/2)(-\epsilon/kT)^{1/2} e^{+\epsilon/kT}]\, r^2\, \mathrm{d}r \quad (11)$$

Introduction of the translational partition functions Q_X, Q_M and Q_{XM} leads to an expression for the equilibrium constant, K_4

$$K_4 = Q_{XM}Q_{\text{int}}/Q_X Q_M = 16\pi^{1/2} \text{ (same integral)} \quad (12)$$

In the integrands in eq. 11 and 12 the erf and exp functions are expanded in series and coefficients of $(\epsilon/kT)^{\text{m}}$ collected.

$$K = 8\pi^{1/2} \int_{\sigma}^{\sigma_1} (-\epsilon/kT)^{1/2} \sum_{m=1}^{\infty} \sum_{l=0}^{m} [(-1)^{m-l}/l!\,(m-l)!(2l+1)](\epsilon/kT)^m r^2 \mathrm{d}r \quad (13)$$

Substitution into the Lennard-Jones potential of the variable $u = (r/\sigma)^3$ allows eq. 13 to be written in the abbreviated, dimensionless form

$$K/\sigma^3 = (8\pi^{1/2}/3) \sum_{m-1}^{\infty} |\alpha_{\text{m}}| I_{\text{m}} (\epsilon_0/kT)^{m+1/2} \quad (14)$$

with $\alpha_{\text{m}} = 4^{m+1/2} \sum_{l=0}^{m} (-1)^{m-l}/l!(m-l)!(2l+1)$ and

$$I_{\text{m}} = \int_{1}^{(\sigma_1/\sigma)^3} (u^{-2} - u^{-4})^{m+1/2}\, \mathrm{d}u$$

It now appears that even if σ_1 is as small as 2σ or less the error introduced by replacing σ_1 by ∞ is inconsequential. The α_{m} are universal coefficients, whereas the I_{m} depend on the form of the interaction potential.

The coefficients in eq. 14 were evaluated up to α_{19} and I_{19} and K/σ^3 calculated as function of ϵ_0/kT to as high a value of the latter as would cause the 19-term series to converge satisfactorily.[16] The results are shown in Fig. 1. For most of the recombination reactions whose rates have been measured, only the $m = 1$ and 2 terms are important; a useful approximate formula is

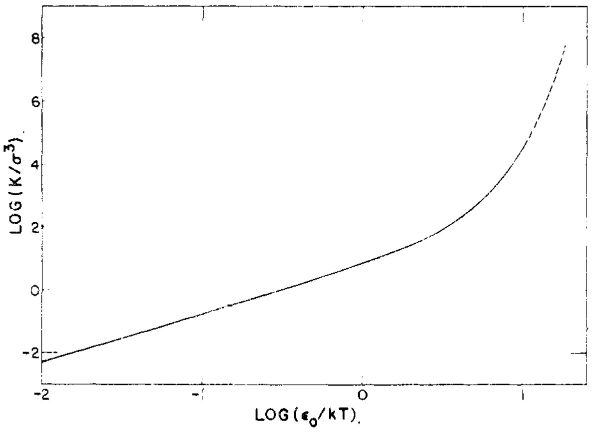

Fig. 1.—Calculated variation of K/σ^3 with ϵ_0/kT.

$$K/\sigma^3 = \pi^{1/2} (\epsilon_0/kT)^{3/2} \left(\frac{8}{3} + \frac{32}{45} \epsilon_0/kT \right) \quad (15)$$

Many of the familiar aspects of recombination rates can be seen on inspection of eq. 15. When combined with the $T^{1/2}$ temperature dependence of the collision number (*cf.* eq. 5), the R.H.S. will exhibit the observed approximately $T^{3/2}$ variation with T. The magnitude of K is a strong function of the intermolecular potential constants; furthermore, it will decrease with increasing temperature most rapidly when ϵ_0^{XM}, and therefore the room temperature recombination rate, is large.

Comparison of Prediction with Observation.—The K and Z appearing in eq. 6 may now be calculated for any third body whose Lennard-Jones parameters are known. For the purpose of comparison with the results of Russell and Simons,[6] we determine, for a particular M, the rate of recombination of I atoms *relative to that in argon;* this tends to diminish uncertainties as to whether the Russell and Simons rate constants may contain small inaccuracies arising from the contribution of I_2 as a third body. The potential parameters required were obtained from Hirschfelder, *et al.*[17] The cross section factor in the collision number was taken as that of X or M, whichever was larger.

Table I exhibits the comparison, at 20°, for all the non-polar gases which are listed in Hirschfelder's tables and were studied in ref. 6. For the most part the agreement is quite good.

TABLE I

CALCULATED AND OBSERVED RELATIVE RATE CONSTANTS

M	$k_R(M)/k_R$(argon) Calcd.	$k_R(M)/k_R$(argon) Obsd.	Ratio obsd./calcd.
He	0.071	0.47	6.6
Ne	0.28	0.50	1.8
A	1	1	1
Kr	1.3	1.2[a]	0.92
Xe	1.9	1.6[a]	0.84
H_2	0.27	1.3	4.8
N_2	0.93	1.2	1.3
O_2	1.0	1.8	1.8
CO_2	2.4	3.7	1.5
CH_4	1.4	2.4	1.7
C_3H_8	5.4	8.4	1.6
n-C_5H_{12}	7.8	13	1.7
Cyclo-C_6H_{12}	9.0	15	1.7
C_2H_4	2.4	4.7	2.0
C_6H_6	7.8	24	3.1
CCl_4	7.7	14	1.8

[a] Ref. 3.

For the third bodies argon and n-butane, for which extensive temperature dependence data are available,[5,7] the comparisons are displayed in Figs. 2 and 3, respectively. The results of the calculation described above are depicted by the solid lines. The agreement with observation is striking. The Lennard-Jones parameters used were: $(\epsilon_0^{\text{IA}}/k) =$

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(16) A Datatron digital computer was employed. I_{m} was evaluated as $2^{2m-1}(2m)!\,(2m+1)!/m\,(4m+1)!$. For $(\epsilon_0/kT) = 10$, the results shown in Fig. 1 are accurate to 0.1%; for $(\epsilon_0/kT) = 15$, to 6%.

(17) 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, pp. 1110–1112.

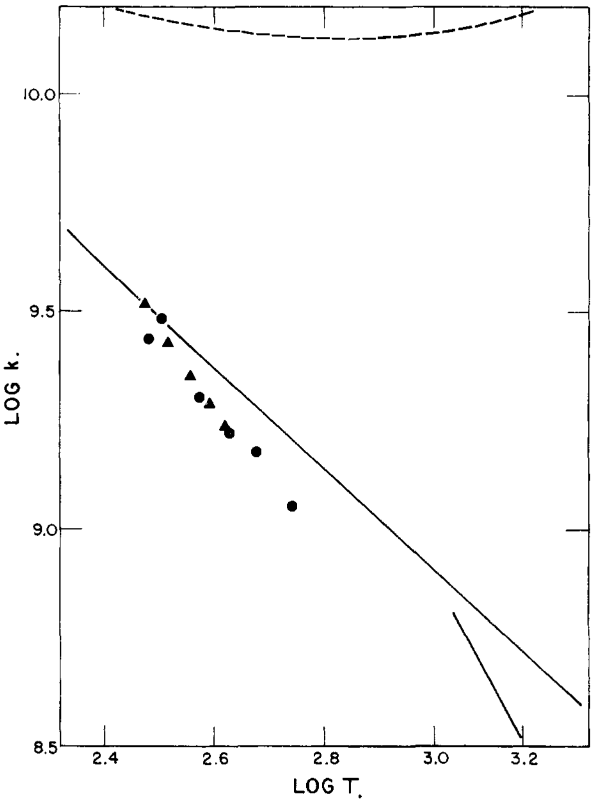

Fig. 2.—Temperature dependence of rate of I + I + A → I_2 + A. Experimental points: circles, ref. 5; triangles, ref. 4; short line segment, ref. 7. Solid line, predicted dependence for bound IA mechanism. Dashed line, predicted dependence for bound plus unbound IA mechanism.

164°, $(\epsilon_0^{\mathrm{IBu}}/k) = 259°$, $\sigma_{\mathrm{IA}} = 3.73$ Å., $\sigma_{\mathrm{IC_4H_{10}}} = 4.97$ Å. The collision numbers used were: $Z_{\mathrm{I-IA}} = 1.04 \times 10^{11} (T/298)^{1/2}$ mole^{-1} liter sec.$^{-1}$, $Z_{\mathrm{I\text{-}IBU}} = 1.66 \times 10^{11} (T/298)^{1/2}$.

For some other gases listed in Table I, high temperature data are available as a result of the shock tube investigation.[7] Table II shows the comparison for these cases.

TABLE II

CALCULATED AND OBSERVED RATE CONSTANTS AT HIGH TEMPERATURES

Third body, M	Temp., °K.	Predicted k_R	Obsd. k_R, l.^{2} mole^{-2} sec.$^{-1}$
He	1400	3.4×10^7	1.8×10^8
N_2	1300	0.84×10^9	0.44×10^9 unrelaxed
			0.71×10^9 relaxed
O_2	1275	0.98×10^9	0.53×10^9
CO_2	1120	3.6×10^9	0.93×10^9

At 25°, Strong, *et al.*,[4] report $k_R = 3.7 \times 10^9$ (l./mole)^2 sec.$^{-1}$ for the recombination of Br atoms in argon (with their apparatus producing "high" results and with no correction for participation of Br_2 as a third body). The shock wave result[8,9] at 1600°K. is 3.4×10^8. Calculation gives 2.6×10^9 (298°K.) and 4.1×10^8 (1600°K.).

It seems to us that in general the agreement between our theory and experiment is satisfactory, except for the cases of He and H_2, both as regards the temperature dependence of k_R and its variation with M.

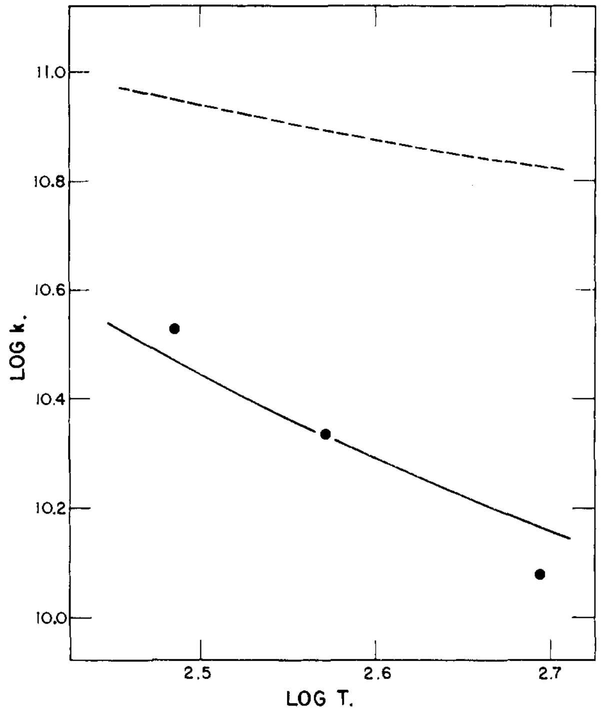

Fig. 3.—Temperature dependence of rate of I + I + n-C_4H_{10} → I_2 + n-C_4H_{10}. Circles, experimental points (ref. 5). Solid line, predicted dependence for bound IC_4H_{10} mechanism; dashed line, predicted dependence for bound plus unbound IC_4H_{10} mechanism.

Further Discussion.—In the preceding sections, we have calculated the concentration of those molecules which have total internal kinetic energy less than their potential energy. Some of this kinetic energy is rotational and some is vibrational. The former is effective in dissociating the MX complex only insofar as there is centrifugal stretching. Therefore, there are molecules in metastable states with total internal kinetic energy greater than their potential energy, but in a configuration inside the "rotational barrier" or maximum in the effective potential energy curve for a rotating molecule. However, the number of molecules in metastable states is rather small compared to those in bound states. That this is the case can be seen approximately as follows. Suppose a molecule has only rotational energy, $p^2_\theta/2\mu r^2$, where p_θ is the rotational angular momentum. If the centrifugal force, $p^2_\theta/\mu r^3$, must be less than the attractive force derived from the potential, $\epsilon(r) = -4\,\epsilon_0(\sigma/r)^6$, it is necessary that

$$p^2_\theta/2\mu r^2 < 3\epsilon(r) \qquad (16)$$

That is, even with all the kinetic energy in rotation, the molecule can have only three times as much kinetic energy as potential.

A more exact answer is now possible. Since this paper was first prepared and submitted, Stogryn and Hirschfelder[18] have actually calculated equilibrium constants, K_b and K_m, for the formation of molecules in bound and metastable states for a

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[18] D. E. Stogryn and J. O. Hirschfelder, "The Contribution of Bound, Metastable, and Free Molecules to the Second Virial Coefficient," Wis-onr-32, N7onr-28511, 15 March, 1958 (University of Wisconsin).

Lennard-Jones potential. Their values for K_b agree exactly with ours. The ratio K_m/K_b is small for $(\epsilon_0/kT)<1$. For example, for butane–iodine, at 32 and 220°, $K_m/K_b = 0.30$ and 0.19. For argon–iodine at 27 and 275°, $K_m/K_b = 0.20$ and 0.12. The assumption that these metastable molecules could react with X atoms by (5) to give recombination would have a very small effect on the calculated rates shown in Figs. 2 and 3. The distinction between molecules in bound and unbound states also has been made by Hill.[19]

We may now consider what sort of results would be obtained if all MX complexes, including those in unbound states, could react with X atoms to give recombination. The molecule is now said to exist in all of momentum space and in a sphere in configuration space of radius r_1. This corresponds to the assertion that for recombination purposes any X and M closer together than an arbitrary distance r_1 should be counted as a molecule, regardless of their relative velocity or whether or not they are "bound" in the usual sense. This definition of a molecule is similar to that used in virial coefficient theory.

The phase integral becomes

$$Q_{\text{int}} = 4\pi \int_0^\infty \int_0^\infty \int_0^\infty e^{-p^2/2\mu kT}\, \mathrm{d}p_x \mathrm{d}p_y \mathrm{d}p_z \int_0^{r_1} e^{-\epsilon/kT}\, r^2 \mathrm{d}r \tag{17}$$

and the equilibrium constant

$$K = (4\pi N/1000) \int_0^{r_1} e^{-\epsilon/kT}\, r^2 \mathrm{d}r \text{ l. mole}^{-1} \tag{18}$$

The integral in (18) has in effect already been evaluated in tables of the second virial coefficient for the L.-J. potential[20]

$$B = (2\pi N/1000) \int_0^\infty (1 - e^{-\epsilon/kT})\, r^2 \mathrm{d}r \tag{19}$$

From (18) and (19)

$$K = -2B + 4\pi(N/1000)r_1^3 + 4\pi(N/1000) \int_{r_1}^\infty (1 - e^{-\epsilon/kT})\, r^2 \mathrm{d}r \tag{20}$$

The integral in (20) is a small negative term; the distance r_1, although not well-defined, is presumably somewhat greater than the L.-J. parameter r_0 ($r_0 = 2^{1/6}\,\sigma$, the separation at the minimum of the potential curve). We make the approximation that the sum of the integral and the small positive quantity $4\pi(N/1000)(r_1^3 - r_0^3)/3$ may be neglected, so that $K = -2B + 4\pi(N/1000)r_0^3/3$.

If we calculate the rates of I + I + A and I + I + C_4H_{10}, using the K derived above in eq. 6 along with the same P, Z, ϵ_0 and σ as previously, we arrive at the dashed lines shown in Figs. 2 and 3. The rates calculated are roughly an order of magnitude greater than those observed. Although the relative efficiency of A and C_4H_{10} is accurately predicted, the mechanism which includes both reactions 5 and 16 gives rise to a predicted temperature variation which is almost completely negligible. The experimental evidence thus seems to indicate that reaction of I with MI* occurs no more often than about 1 in 10^2 collisions, and does not compete with reaction 5 in Br and I recombination.

The other possible model which should be considered is that expressed by equations 2 and 3. As pointed out previously,[11,12] this leads to

$$k_R = Z_{I-I}\, \tau P_3 Z_{I_2^*-M} \tag{21}$$

where τ is the lifetime of I_2^*. Taking τ as the harmonic vibration period of I_2 in its ground electronic state, and suitable collision numbers, one obtains

$$\begin{aligned} k_R &= 1.6 \times 10^9\,(T/298)P_3 \text{ for M} = \text{A} \\ &= 2.7 \times 10^9\,(T/298)P_3 \text{ for M} = C_4H_{10} \end{aligned} \tag{22}$$

The results for argon are of the correct order of magnitude if $P_3 \sim 1$. For butane, one must assume $P_3 \sim 10$ which is unreasonable. Furthermore, it is necessary to assume arbitrarily that P varies as $T^{-2.3}$ and $T^{-3.2}$ in (22) to duplicate the observed temperature dependence. It may be that a more detailed theory—perhaps considering the effects of collisions with appreciable angular momentum on τ, perhaps calculating the probability of vibrational deactivation of I_2^* (P_3) in the same spirit as in the quantum mechanical treatment of vibrational relaxation[21]—would explain the data.

It has been suggested[22] that a more realistic way of estimating τ for I_2^* is to use a Morse curve for the I–I interaction and to say that there is an I_2^* molecule capable of reacting according to (3) when the I–I distance is such that the negative of the potential energy is greater than kT. The results of this calculation will be reported by Dr. Keck. We note here that the decrease in collision radius with increasing temperature does not provide a sufficiently great negative temperature coefficient to agree with the experimental data. Furthermore, the large difference between argon and butane is not explained.

Another serious question in this whole field is that of electronic degeneracy. The total degeneracy of two ground state $^2P_{3/2}$ iodine atoms is 16. The degeneracy of the molecular ground state ($^1\Sigma$) is (1). Does this mean that we should introduce an additional steric factor of 16, which would make our calculated rates much less than the observed rates? The question has been discussed by Rabinowitch.[11] The only other known stable molecular state resulting from $^2P_{3/2}$ atom is $^3\Pi_1$, with $g = 3$. The dissociation energy of this state is ~ 1850 cal. The rate constant for dissociation of normal molecules is $k_D \sim 40Z \exp(-\Delta E/RT)$[12] ($Z$ being a kinetic theory collision number). By analogy, a molecule in the $^3\Pi_1$ electronic state would dissociate on about every collision at room temperature. Therefore, in the competing reactions

$$I_2(^3\Pi_1) + M \longrightarrow I_2(^1\Sigma) + M \tag{22a}$$

$$I_2(^3\Pi_1) + M \longrightarrow I + I + M, \tag{22b}$$

the latter is probably the faster and the $^3\Pi_1$ state is not important for recombination. There may be some other bound potential states which have not been observed spectroscopically.[11] In any case, Rabinowitch concluded that for atoms like iodine with strong spin-orbit coupling, the spin conservation rules were not very strong and that it was better to omit the steric factor of 16. Presumably

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(20) J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, ref. 17, pp. 1110–1115.

(21) R. N. Schwartz and K. F. Herzfeld, *J. Chem. Phys.*, **22**, 767 (1954).

(22) J. Keck, private communication.

the spin selection rules should hold rather well for the recombination of light atoms; the question of their application for iodine atoms is an important, unanswered question.

Finally, it is worth noting that while the assumption that only MX's in bound states can react with X to give X_2 is essentially *ad hoc*, it is rather reasonable. It is intuitively plausible that, in such a complex, the M–X coupling is relatively strong so that the M atom may receive a strong impulse and carry away kinetic energy when another X approaches. This is less likely for MX complexes in unbound states, where the kinetic energy is larger than the potential energy.

Light Third Bodies.—In case the third body is H_2, D_2 or He, there are too few energy levels of the complex XM for the phase integral form of Q_{int} to be used. This restriction would also apply to H or D atoms recombining in the presence of any third body. The treatment outlined above is therefore not quantitatively applicable. Qualitative predictions can however be made. The equilibrium constant for the formation of the complex $I_2 \cdot H_2$ or $I_2 \cdot$He would be expected to be quite small because of the smallness of ϵ_0. Yet, for I atom recombination, H_2 is slightly more efficient than A as a third body. This suggests that one of the other above mechanisms contributes to the recombination. If it be that involving reactions 2 and 3, P_3 must vary with mass as $m^{1/2}$ since there is no isotope effect for H_2 and D_2, and the collision factor in (21) contributes a factor of $2^{-1/2}$ to $k(D_2)/k(H_2)$. Measurements of the temperature coefficient for He and H_2 are being undertaken in this Laboratory.

Chemically Bound XM: The I_3 Molecule.—The remarkable efficiency of I_2 as a catalyst (k/k(argon) = 650 at 298°K.[5] or 250 at 295°K.[3]) is most reasonably attributed to the formation of I_3. This presumably involves valence forces and not the non-specific dispersion forces considered previously.

Obviously the I_2^* mechanism, which constructs the efficiences of various M largely on the basis of their collision diameters, can never account for the 650-fold difference between the rates of I + I + A and I + I + I_2 observed at room temperature. Also, the negative temperature coefficient of the latter is extremely large for a recombination reaction, and this is most easily attributed to the effect of temperature on the equilibrium

$$I + I_2 = I_3 \tag{23}$$

To facilitate discussion of the latter question, we write the complete reaction scheme

$$I + I_2 = I_3^* \tag{24}$$

$$I_3^* + M = I_3 + M \tag{25}$$

$$I_3 + I \longrightarrow 2I_2 \tag{26}$$

I_3^* is an energized molecule in the sense of unimolecular reaction rate theory. Reactions 24 are surely fast, and the usual kinetic analysis indicates that the requirement for an equilibrium concentration of I_3 is that $k_{-25}(M) >> k_{26}(I)$. Assume that k_{26} and k_{25} are equal to a collision number Z. Application of the classical version of the Rice–Kassels theory then gives $k_{-25} = Z(E_0/RT)^{s-1} \cdot (1/(s-1)!)e^{-E_0/RT}$, where E_0 = 5320 cal. (see below) and s is 3 or 4 depending on whether I_3 is bent or linear. One thus obtains $k_{-25} = 0.02Z$ (s = 4) or $0.005Z$ (s = 3). In our experiments[5] (M)/(I) > 2500 always, so $k_{-25}(M)/k_{26}(I) > 12.5$ always. Thus the assumption of an equilibrium amount of I_3 was justified in our experiments, although it might not be in cases where lower (M)/(I_2) and higher degrees of photodissociation were employed. The measurements of the rate of I + I + I_2 may safely be regarded as giving information about the equilibrium 23. Combination of the *observed* rate[5] with a collision number and P = 1, in eq. 6 yields

$$K = 7.7 \times 10^{-5}\, e^{5320/RT} \text{ atm.}^{-1} \tag{27}$$

from which, for reaction 23, ΔS^0 = 20 e.u. and ΔH = − 5320 cal.

For comparison purposes, an approximate statistical calculation of the entropy of I_3 may be made. If we take a linear half-bonded molecule[23] with L(I–I) = 2.75 Å. and frequencies ν_1 = 120 cm.$^{-1}$, ν_2 = 80 cm.$^{-1}$ (doubly degenerate), and ν_3 = 210 cm.$^{-1}$, we predict, for reaction 23, ΔS = −25 e.u. In view of the uncertain assumptions, this calculation merely indicates that the "experimental" value for the entropy of (23) is not unreasonable. For ΔH a calculation by the semi-empirical method leads to a value of 2400 cal.[24]

The magnitude of the equilibrium constant indicates that under ordinary conditions I_3 is largely dissociated and that it will not be an important intermediate in most photochemical reactions. Arguments for the general unimportance of reaction mechanisms involving triatomic halogen molecules have been summarized by Steacie.[25]

Several other comments about chemically bound XM's can be made. In the plot of k_R *vs.* boiling point[6] several molecules fall above the straight line through the majority of data. These include aromatic hydrocarbons such as toluene and mesitylene (and possibly a small effect in benzene). On the basis of the well known complex formation with I_2, a chemical interaction with an I atom is expected. There is evidently a special interaction with ethyl iodide also.

Conclusion.—In general this paper has favored the XM hypothesis for the recombination of halogen atoms. In the case of I_3, the experimental data so interpreted lead to a reasonable value for the entropy of this species and a value of −5300 cal. for its ΔH of formation from I and I_2.

When M is chemically inert, MX is a van der Waals complex. The concentration of MX can be calculated using data on intermolecular potentials. The arbitrary assumption that MX can react with X to give X_2 only if MX is in a bound state leads to a good agreement with the data, both as regards the variation of k_R with T and with M.

The recombination rate for M = H_2 and He are not explained by this mechanism. Further data on the rate constants and their temperature coefficients for these molecules are needed. It may be

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(24) G. K. Rollefson and H. Eyring, *ibid.*, **54**, 170 (1932).

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that when a theory that explains these cases is formulated, it will also be applicable to the case of the heavier third bodies. However, the theory advanced here is sufficiently successful that we feel justified in advancing it at the present time.

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Pasadena, Calif.

[Contribution from Coates Chemical Laboratories, Louisiana State University, and the Department of Chemistry, The Florida State University]

Energy Transfer in Molecular Complexes of *sym*-Trinitrobenzene with Polyacenes.
I. General Considerations[1]

By S. P. McGlynn[2] and J. D. Boggus

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The emission spectra of π-complexes of aromatics with *sym*-trinitrobenzene have been studied. It is shown that after irradiation in the charge-transfer band, two emissions occur: one the reverse of the charge-transfer absorption, the other from a triplet level of the uncomplexed aromatic. Absorption spectra of complexes, their total emission spectra and phosphorescence emissions are described. Theoretical considerations of the processes involved lead us to presume that after excitation in the charge-transfer band, some intersystem crossing occurs to a dissociative triplet level of the complex. The resultant production of uncomplexed aromatic in its lowest triplet state then gives rise to the observed phosphorescence. State correlation diagrams and plots of ionization potential of aromatic *versus* the energy of the charge-transfer absorption are also described.

Introduction

The origin of the emission spectrum characteristic of many π-complexes of *sym*-trinitrobenzene (TNB) with aromatics is to a large extent uncertain. Reid[3] observed a general parallelism of the emission spectra of such complexes with the T → S luminescence of the free uncomplexed aromatic component; since the anthracene–TNB complex had an emission extending from 5200 Å. into the infrared, he assigned, on the basis of the above parallelism, an energy of 19000 cm.$^{-1}$ to the lowest triplet state of anthracene. An energy of 14700 cm.$^{-1}$ already had been assigned to this state by Lewis and Kasha,[4] and this value was later affirmed[5] by vibrational analyses of the phosphorescence spectra of anthracene and its derivatives. Despite this exception of the anthracene–TNB complex, the great majority of the other complexes studied[6] did have emissions corresponding almost exactly to the T → S luminescence of the aromatic components. Indeed the remarkable spectral coincidence was interpreted as meaning that the triplet level of the aromatic was almost unaffected energy-wise in the complexing process.[7,8]

Bier and Ketelaar[9] noted that the emission and absorption spectra of both anthracene–TNB and phenanthrene–TNB were approximate "mirror images." They concluded that both processes involved the same two levels, that is that the emission process was the reverse (E → N) of the charge-transfer absorption (E ← N). This suggestion, however, did not meet with a general acceptance.[10] More recently Czekalla, Briegleb and collaborators[11] have extended the work of Bier and Ketelaar. These authors investigated the molecular compounds of hexamethylbenzene with each of eight different acceptor molecules ("acceptor" in the Lewis acid–base sense). The charge-transfer absorption of the complex shifted to the red as the electron affinity of the acceptor component increased; and the emission spectrum red-shifted similarly so that in each case the "mirror-image" relation was maintained. There remains then but little doubt that, at least for complexes of hexamethylbenzene, the emission is a charge-transfer (E → N) emission.

For the particular complex tetrachlorophthalic anhydride–naphthalene it was possible[11] because of a large spectral separation, to distinguish two emissions after excitation with Hg 3650: one the reverse of the charge-transfer absorption with half life $\tau = 10^{-9}$ sec, and the other corresponding to the phosphorescence of naphthalene with an unchanged half-life of a few seconds.[12,13]

In view of these experimental results, a reasonable interpretation would seem to be: absorption in the charge-transfer band is followed either by the converse emission, or by intersystem crossing[14] to a

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[1] Portions of this research are taken from S. P. McGlynn. Ph.D. Dissertation, The Florida State University, Jan., 1956, and J. D. Boggus, M.S. Thesis, The Florida State University, Jan., 1956. The research was done under Contract AF-18(600)-678 between the Office of Scientific Research, U. S. Air Force, and the Florida State University.

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[8] It was assumed, of course, that emission occurred from a triplet level of the complex which was approximately described as a product of the ground state wave function ($^1A_{1g}$) of TNB and the first excited triplet state ($^3B_{2u}$) of anthracene. The energy of this level of the complex was supposed to be only slightly different from its energy at infinite separation of the components.

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