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Author

Genser, Edward E.

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THE EXCHANGE OF IODIDE ION WITH TRIIODIDE ION STUDIED
BY NUCLEAR MAGNETIC RESONANCE

Edward E. Genser^{*} and Robert E. Connick

Inorganic Materials Research Division, Lawrence Berkeley Laboratory and
Department of Chemistry; University of California,
Berkeley, California 94720

ABSTRACT

Previous studies of NMR line broadening of the iodide resonance in aqueous solutions of triiodide have been interpreted in terms of the rate of dissociation and formation of triiodide, with the result that the derived rate constant appeared to exceed the diffusion limiting value. The present study has resolved this anomaly and shows the exchange to be described instead by the reaction:

at iodide concentrations greater than 0.05 M.

Several mechanisms of exchange are considered based on both symmetrical and unsymmetrical forms of triiodide ion, the latter of which is supported by Raman data in the literature. The interpretation makes use of nuclear quadrupole coupling constants reported for solid salts of triiodide. The data are fitted to the exchange modified Bloch equation to obtain a value of the rotational correlation time, τ_r , for each of the mechanisms; τ_r is then compared to a theoretical value of τ_r calculated for triiodide ion. Although the data do not permit a unique

mechanism to be established, it appears that at least two of the iodines in triiodide must be involved in exchange. The results are compatible with an attack on an end iodine of triiodide with the formation of the intermediate I_4^{2-} .

Myers¹ has used the measurement of the linewidth of the nuclear magnetic resonance of iodine-127 in iodide solutions containing triiodide ion to yield information on the rate of exchange of iodine nuclei between the two species. The I^{127} nucleus, when present as I^- in an aqueous solution, undergoes transverse relaxation through quadrupole coupling with the surrounding water molecules at a rate which produces a conveniently measurable resonance linewidth. The same nucleus, when present in I_3^- , relaxes much more rapidly because of the much stronger quadrupole coupling. Therefore, the presence of a small amount of triiodide ion causes measurable broadening of the I^- resonance linewidth through chemical exchange.

Myers interpreted the concentration dependence of the line broadening in terms of the rapid formation and dissociation of triiodide ion:

From the results of his study he deduced a value for k_f of $4.7 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ at 35°C . However, estimates^{2,3} of the diffusion controlled bimolecular rate constant⁴ for this reaction at the same temperature give a value for k_f of only $1.8 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$. The work reported here was undertaken with the hope of resolving this discrepancy. Our initial measurements at 27°C appeared to be consistent with Myers' rate law and moreover yielded an even larger value of k_f . Further measurements, however, of the concentration and temperature dependences of the line broadening revealed a more complicated exchange mechanism.

EXPERIMENTAL

The techniques and theory of the measurement of rapid rate processes through NMR line broadening have been amply treated elsewhere^{5,6,7}. The experiments were performed on a Varian V4200B spectrometer at 8.00 Mhz which corresponds, for I^{127} , to a field of 9.4 Kgauss. The iodide ion linewidths are peak-to-peak separations of the absorption derivative. For solutions of potassium iodide at 2M (moles per liter) and below, the line width was constant at 1.15 gauss. The line shapes were Lorentzian to a good approximation, for which the expression $\frac{1}{T_2} = (\frac{\sqrt{3}}{2})\gamma\Delta H$ applies, where γ is the nuclear gyromagnetic ratio, ΔH is the linewidth in gauss, and T_2 is the transverse relaxation time. Field sweeps were calibrated using the sidebands impressed on water protons at 40 Mhz. The amplitudes of the modulation and radiofrequency fields were set well below the levels which produce observable broadening.

The iodide salt was weighed out directly and the triiodide concentrations were measured spectrophotometrically by using the molar extinction coefficient of I_3^- at the absorption maximum at 3530 Å⁸. The pure iodide solutions were made 10^{-3} M in $Na_2S_2O_3$ to prevent oxidation. The linewidths were independent of ionic strength below 2M apart from the small effects attributed to ion pairing with the specific alkali metal cation⁹. All solutions containing 0.1, 0.4, 1.0 and 2.0 M I^- were at a constant ionic strength of 2.00 M, achieved by adding $NaNO_3$ to the KI and I_2 . All other solutions had an ionic strength equal to the iodide concentration (KI). The temperature dependences were studied with an apparatus described elsewhere⁷, consisting of a pyrex cell with a glass

coil immersed in the sample, through which a gas was passed for heat exchange.

The spectrophotometric measurement of the I_3^- concentration requires further comment. Chia¹⁰ and French and Effenberger¹¹ have shown that the apparent molar absorptivity of I_3^- varies with the iodide concentration. Chia's data interpolated to 3530 Å and combined with the data of Awtrey and Connick⁸ for low iodide concentrations gives for the molar absorptivity

$$\epsilon^{3530} = 2.64 \times 10^4 (1 + 0.164 [I^-]) \quad (2)$$

up to 1 M I^- . We define the apparent triiodide concentration, $[I_3^-]_{app}$ as

$$[I_3^-]_{app} = \frac{A^{3530}}{2.64 \times 10^4 b} \quad (3a)$$

and the "stoichiometric triiodide", symbol $[I_3^-]'$ as

$$[I_3^-]' = \frac{A^{3530}}{2.64 \times 10^4 b (1 + 0.164 [I^-])} = \frac{[I_3^-]_{app}}{1 + 0.164 [I^-]} \quad (3b)$$

where A is the absorbance and b the cell length.

French and Effenberger have analyzed their data in terms of higher polyiodides and give for the equilibrium quotient for the formation of I_4^{2-} , the next most important species for the conditions used here, at ionic strength 2M(KNO_3) and 25°:

If one accepts their interpretation,

$$[I_3^-]' = [I_3^-] + [I_4^{2-}] \quad (5)$$

RESULTS AND DISCUSSION

In Figure 1 a plot of the line broadening δ (in gauss) versus $[I_3^-]_{app}$ at 2M iodide concentration is shown. The value of the contribution from the pure iodide ion linewidth was subtracted from the measured overall linewidth to obtain δ . Linear plots of this type were also obtained at several other iodide ion concentrations. The linearity establishes that the observed increase in rate of relaxation of I^- arising from the presence of I_3^- is proportional to $[I_3^-]_{app}$ and therefore to $[I_3^-]'$ and also $[I_3^-]$ at a given iodide concentration. The slopes of the linear plots, such as Figure 1, were measured and multiplied by $(\frac{\sqrt{3}}{2})\gamma$ to give the second order rate constants for the enhanced I^- relaxation, shown in Table 1, according to:

$$(\frac{\sqrt{3}}{2})\gamma\delta = \frac{1}{[I^-]} \frac{d[I^-]}{dt} = k_1[I_3^-]' = k_2[I_3^-] \quad (6)$$

The evaluation of k_2 requires the additional assumption of the presence of the I_4^{2-} species and the applicability of French and Effenberger's equilibrium quotient for equation (4) to the present system, $k_2 = k_1(1 + 0.184 [I^-])$ at room temperature. At low $[I^-]$, k_2 approaches k_1 .

Obviously k_1 and k_2 are not constant. Values of the reciprocal of each plotted against $[I^-]$ in Figure 2 indicates that to a first approximation they are inversely proportional to the iodide concentration.

Thus the simplest approximate rate law for the enhanced relaxation of I^- is

$$\frac{-d[I^-]}{dt} = k_3 \frac{[I^-][I_3^-]'}{[I^-]} = k_4 \frac{[I^-][I_3^-]}{[I^-]} = k_4 Q_{I_3^-} [I^-][I_2] \quad (7)$$

where $Q_{I_3^-}$ is the equilibrium quotient for the formation of I_3^- .

TABLE I

Relaxation Data for I^- in Solutions Containing I_3^- at 27° C.

$[I^-], M$	$\mu^\dagger, M$	$\frac{1}{k_0}, M \text{ sec}$	$\frac{1}{k_1}, M \text{ sec}$	$\frac{1}{k_2}, M \text{ sec}$
0.050	.05	0.85×10^{-9}	0.84×10^{-9}	0.83×10^{-9}
0.100	2.00	0.92	0.90	0.89
0.400	2.00	2.65	2.49	2.32
1.00	2.00	7.25	6.23	5.26
2.00	2.00	17.4	13.6*	10.0
3.00	3.00	25.1		
4.00	4.00	34.0		
5.00	5.00	43.		
6.00	6.00	48.		

*Eq. (2) is a first order empirical correction to the molar absorptivity for the presence of higher polyiodides, valid up to 1M iodide. A more exact treatment based on the assumed presence of I_4^{2-} was used to calculate ϵ^{3530} at $2MI^-$, resulting in a 4 percent higher value of $[I_3^-]$ than given by Eq. (3b).

[†]Ionic strength.

This is exactly the rate law for the relaxation found by Myers¹ and interpreted by him as the rate of dissociation and formation of triiodide ion.

The key to the problem was revealed by a study of the temperature dependence of the relaxation. In Figure 3 is shown a plot of $\log([I^-]\delta/[I_3^-]_{app})$ versus $1/T$ for several iodide concentrations at and above 0.4M. The contribution from the pure iodide ion linewidth — the temperature dependence of which is shown in Figure 4 — has been subtracted from the overall linewidth to obtain the value of δ .

In Figure 3, if the rate of relaxation depended on the rate of dissociation of triiodide ion, the plot would be of the usual Arrhenius type with the rate constant increasing with increasing temperature. Exactly the opposite trend is found with $\Delta E \approx -4.3$ kcal.

In a two environment system with a small difference in chemical shift, the enhancement of relaxation of the first environment by the presence of the second is controlled by the slower of the two steps; 1) chemical exchange and, 2) relaxation in the second environment. The temperature dependence data show unequivocally that the former is not controlling under the conditions in Figure 3.

If relaxation is the controlling step the rate is proportional to the rate of relaxation in the second environment:

$$\frac{-d[I^-^*]}{dt} = k'[I_3^-^*] = k''Q_{I_3^-}[I^-^*][I_2] \quad (8)$$

which is just the form found experimentally, to a good approximation. With relaxation control dominating at 0.4M I^- and higher, chemical exchange must be faster than the relaxation. The triiodide dissociation and recombination mechanism for the exchange becomes even more impossible with this new interpretation. The system must effect an exchange of iodine atoms between I_3^- and I^- considerably more rapidly than the

diffusion controlled bimolecular reaction rate limit for Equation (1). The only reasonable possibility appears to be the direct bimolecular reaction:

At the diffusion limit this reaction theoretically could produce exchange at approximately $Q_{\text{I}_3^-} [\text{I}^-]$ times the rate of exchange through $\text{I}^- + \text{I}_2$. This would correspond to a rate which is 714 times greater for a one molar iodide solution at 25° C.

By a suitable change in the experimental conditions it should be possible to make chemical exchange the controlling factor. The above mechanism for such a situation gives:

$$\frac{-d[\text{I}^{\ast-}]}{dt} = k_5 [\text{I}^{\ast-}] [\text{I}_3^-] \quad (10)$$

It will be shown below (Equation 13) that chemical exchange control will be favored (low relative rate) by low iodide concentration. Consideration of the temperature dependence shows that low temperature will also favor chemical exchange control since decreasing the temperature will decrease the rate of chemical exchange but increase the quadrupole relaxation of I_3^- because of the longer correlation time from tumbling.

Attempts to gain evidence of chemical exchange control were carried out as follows. First, measurements were made at 27° C with decreasing concentrations of iodide ion down to 0.05 M at which point the small signal to noise ratio precluded further decrease. As will be explained later, chemical exchange control according to Equation (10) should manifest itself in Figure 2 as a finite intercept on the ordinate axis.

Such a result was obtained although the accuracy is not high.

Secondly, the temperature dependence was measured at low iodide ion concentration (0.05 M), as shown in Figure 5. The sign of the temperature dependence is now reversed from that found at 0.4 M and higher iodide concentrations, thus confirming the presence of chemical exchange control. The low value of the activation energy indicates, as would be expected, that exchange control is only slightly more important than relaxation control under the conditions of the experiment.

We now wish to establish an explicit relationship between the resonance linewidth of the iodide ion and the pertinent rate and relaxation parameters. We consider the special solution of the exchange modified Bloch equations for two site exchange with one component in low abundance. The quantity $1/T_{2p}$ is given in terms of the line broadening, δ , by:⁷

$$1/T_{2p} = \left(\frac{\sqrt{3}}{2}\right) \gamma \delta = \frac{1}{\tau_c} \left\{ \frac{\frac{1}{T_{2d}^2} + \frac{1}{T_{2d}\tau_d} + \Delta\omega_d^2}{\left(\frac{1}{T_{2d}} + \frac{1}{\tau_d}\right)^2 + \Delta\omega_d^2} \right\} \quad (11)$$

where τ_d , T_{2d} and $\Delta\omega_d$ are respectively the chemical lifetime, transverse relaxation time and chemical shift of the iodine in species d. We make the identification of the species c with iodide, whose resonance we are observing, and d with triiodide. The specific processes are:

with $\frac{1}{\tau_c} = k_5[I_3^-]$ and $\frac{1}{\tau_d} = k_6[I^-]$

We can simplify Equation (11) by noting that the chemical shift $\Delta\omega_d$ is an ordinary diamagnetic shift which is small in comparison to the relaxation and exchange rates, and may therefore be ignored, i.e., the chemical shift is much less than the line broadening. Then Equation (11) becomes

$$\frac{1}{T_{2p}} = \frac{1}{\tau_c} \times \frac{\tau_d}{T_{2d} + \tau_d} = \frac{k_5[I_3^-]}{k_6[I^-]T_{2d} + 1} \quad (13)$$

Equation (13) displays, very simply, the line broadening as a function of the chemical and magnetic lifetimes of an I^{127} nucleus in triiodide. For very rapid chemical exchange one has a relaxation controlled width, i.e., for $(\tau_d/\tau_{2d}) \ll 1$:

$$\frac{1}{T_{2p}} = \frac{\tau_d}{\tau_c} \frac{1}{T_{2d}} = \frac{1}{T_{2d}} \frac{k_5}{k_6} \frac{[I_3^-]}{[I^-]} \quad (14)$$

In the limit of slow exchange the line broadening is controlled by the exchange rate, i.e., for $\tau_d/T_{2d} \gg 1$:

$$\frac{1}{T_{2p}} = \frac{1}{\tau_c} = k_5[I_3^-] \quad (15)$$

The experimental data are qualitatively consistent with this description. To proceed further, it is necessary to examine more carefully both the relaxation and the chemical exchange processes.

The nuclear magnetic relaxation of I^{127} occurs by quadrupole coupling. For liquids the expression for $\frac{1}{T_{2d}}$ is of the form:¹²

$$\frac{1}{T_{2d}} = 4\pi^2 \alpha v_q^2 \tau_{eff} = \beta \tau_{eff} \quad (16)$$

Where $v_q = \frac{e^2 q Q}{h}$ is the conventional quadrupole coupling constant in which q is the electric field gradient at the nucleus whose quadrupole moment is Q . The value of α for a nuclear spin of $5/2$ (i.e., I^{127}) is 2.4×10^{-2} . The expression is exact for axial symmetry (which we shall assume), and a very good approximation for small departures therefrom. The quantity τ_{eff} is an "effective" correlation time for the quadrupole coupling given by the expression:

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_r} + k_6[I^-] \quad (17)$$

Here, $\frac{1}{\tau_r}$ and $k_6[I^-]$ are the rates at which the quadrupole coupling is interrupted through rotational motion and chemical exchange, respectively.

The value of τ_r is often estimated from the Debye-Bloembergen model of a randomly rotating sphere embedded in a viscous liquid. Shimizu¹³ has derived the quadrupole relaxation formula for the tumbling of a

symmetrical ellipsoid. It has the same form as Equations (16) and (17) but the rotational part of τ_{eff} is more complex. On estimating major and minor axes of the ellipsoid from interatomic distances of triiodide ion and the van der Waals radius of iodine, one calculates from Shimizu's work a value of τ_r of ca. 4.4×10^{-11} sec. at 25° C. This value is uncertain because the hydrodynamic basis of the model is highly questionable at molecular dimensions¹⁴; a factor of 2 error would not be surprising. Since only rotation about the minor axes is effective in de-correlating the quadrupole coupling of linear I_3^- , the hydrodynamic theory may actually be more appropriate here than for a sphere¹⁵.

Taking the inverse of Equation (13) and substituting for T_{2d} from Equation (16) yields

$$T_{2p} [\text{I}_3^-] = \frac{1}{k_5} + \frac{k_6 [\text{I}^-]}{k_5 \beta} \left(\frac{1}{\tau_r} + k_6 [\text{I}^-] \right) \quad (18)$$

Equation (18) oversimplifies the chemical exchange and relaxation processes. There are three iodine atoms in I_3^- . It is most unlikely that they all exchange at the same rate. Each may have a different quadrupole coupling constant. There is strong evidence that I_3^- in aqueous solution is not symmetrical, although it is probably linear or very nearly so. X-ray structure determinations¹⁶ of solid triiodides have shown I_3^- to be sometimes symmetrical and sometimes asymmetrical with the two different distances from the center to the end iodines, ranging from 2.82 to 2.91 Å for the short distance and 3.10 to 2.95 Å for the long distance. Recent Raman measurements in aqueous solution^{17,18} also indicate two active stretching frequencies, which would only be the case

if the I_3^- were unsymmetrical and retained a given asymmetrical configuration for the order of 2×10^{-12} sec. or longer.

Of great interest here are the quadrupole coupling measurements of Sasane, Nakamura and Kubo¹⁹ on solid NH_4I_3 , RbI_3 and CsI_3 . Three distinct coupling constants were observed for each substance, averaging 710, 1490, and 2,480 Mhz, although the individual values varied appreciably. These are assigned in order to ν_a , ν_b and ν_c of the atoms indicated in unsymmetrical I_3^- , with the a-c bond longer than the c-b bond:

The sum of the three frequencies for each solid is remarkably constant and nearly equal to twice that of the iodine atom,²⁰ as could be expected if only p orbitals are used in bonding, i.e., the molecular orbital model proposed by Pimentel²¹, and if the theory of Townes and Dailey²² is applied.

The exchange process can proceed by attack of the incoming I^- on either the central or one of the end iodines of triiodide. In the first process the incoming I^- replaces an end iodine, without change of the relative positions of the other two. In the second case the incoming iodide attaches to one of the end iodines, which in turn becomes the new center iodine, while the other end iodine is lost as I^- . In addition to the two methods of attack there are other complexities. Both the unsymmetrical and symmetrical structures for I_3^- must be considered. The symmetry of the activated complex (or an intermediate) can affect the exchange. If the triiodide is unsymmetrical, the rate of inversion of the asymmetry can affect the results. Further, when two or more sites

are involved in relaxation the appropriate combination of quadrupole coupling constants must be chosen.

The results of consideration of a number of the more plausible of these alternatives is presented in Table II. Here the cases are classified first by mode of attack and secondly by symmetry of the I_3^- , with the possibility of rapid inversion for the unsymmetrical case. The second column lists the appropriate ratio for k_5/k_6 in equation (18), except where indicated, and the last column gives appropriate expressions for ν_q in equation (16), except where indicated; when alternative expressions are given the first corresponds to rapid exchange between the sites relative to tumbling and the latter case the opposite.

The equation for the transverse relaxation time involving relaxation and exchange can be derived readily using classical kinetic methods of the steady state as long as the chemical shift is small enough not to contribute to the linewidth², which is the case here. In addition, it is necessary that exchange not be rapid compared to the randomizing process, i.e., tumbling in the present case. When this latter condition does not hold, the derivation is more complex.

For attack on the end iodine of symmetrical triiodide the relaxation equation is

TABLE II

Possible Mechanisms for Exchange of I^- with I_3^-

<u>Mechanism</u>	<u>k_5/k_6</u>	<u>v_q^2</u>
A. Attack on center iodine of I_3^-		
1. Symmetrical I_3^-	2	v_{ab}^2 †
2. Unsymmetrical I_3^-		
(a) no inversion	1	v_a^2
(b) rapid inversion	2	$\left(\frac{v_a+v_b}{2}\right)^2$ or $\frac{v_a^2+v_b^2}{2}$
B. Attack on end iodine of I_3^-		
1. Symmetrical I_3^-	Kinetics* more complex	$\left(\frac{2v_{ab}+v_c}{3}\right)^2$ or $\frac{2v_{ab}^2+v_c^2}{3}$ †
2. Unsymmetrical I_3^-		
(a) no inversion	1	v_a^2
(b) rapid inversion	Kinetics* more complex ‡	$\left(\frac{v_a+v_b+v_c}{3}\right)^2$ or $\left(\frac{v_a+v_b}{2}\right)^2 + v_c^2$

† v_{ab} is the quadrupole coupling constant for the end iodines in symmetrical I_3^- .

* See Text and equation (19).

‡ See Text.

$$T_{2p} [I_3^-] = \frac{1}{k_5} + \frac{[I^-]}{\frac{k_5 \beta_{ab}}{k_6(1/\tau_r + 2k_6[I^-])} + \frac{1}{1/(k_5[I^-]) + \frac{1/\tau_r + k_5[I^-]}{\beta_c}}} \quad (19)$$

where β_1 corresponds to the β of equation (16) for the atom indicated by the subscript. This form is only valid when $k_5[I^-]$ is appreciably smaller than $1/\tau_r$, which turns out to be the case up to $1M I^-$. For the unsymmetrical I_3^- with attack on the end iodine a similar equation is obtained if the rate of inversion of the asymmetry is rapid compared to the sum of the relaxation rates in the tightly bound and center positions.

Because of the many possible mechanistic paths, indicated only incompletely in Table I, it is not feasible to use the NMR results to determine uniquely the mechanism of relaxation. To simplify the problem the average quadrupole coupling values of Sasane, Nakamura and Kubo¹⁹ will be used to fix the ν_q parameters in the equation for T_{2p} . Fortunately the two possible averages — the average of the squares and the square of the averages (in Table II) — do not differ greatly. As judged by its constancy in reference 19, $\frac{\nu_a + \nu_b}{2}$ should be a good measure of the quadrupole coupling frequency of the end iodines of symmetrical I_3^- , and is so used in Table II.

Using the above parameters, the data at 0.1 and $1M I^-$ were used to calculate k_5 and $1/\tau_r$ for the various paths in Table II with the results shown in Table III. The first set of results labeled "Based on $[I_3^-]$ " corresponds to assuming approximately that the species forming at higher iodide (presumably I_4^{2-}) contributes to the relaxation in the same degree that an I_3^- does, at one molar iodide. The second set, labeled "Based on $[I_3^-]$ " corresponds to assuming that the species forming at

TABLE III

Kinetic Parameters Calculated for Different Mechanisms

Mechanism (See Table II)	Based on $[I_3^-]'$ [†]		Based on $[I_3^-]$ [†]	
	k_5	$1/\tau_r$	k_5	$1/\tau_r$
A, 1 A, 2, (b)*	2.7×10^9	1.2×10^{10}	2.2×10^9	1.0×10^{10}
A, 2, (a) B, 2, (a)	1.6×10^9	1.1×10^9	1.4×10^9	0.75×10^9
B, 1 B, 2, (b)*	4.1×10^9	4.3×10^{10}	3.3×10^9	3.6×10^{10}

[†] The interpretations based on $[I_3^-]'$ and $[I_3^-]$ correspond to substitution of the k_5 and k_6 data of Table I, respectively, into equations (18) and (19), along with the assumption in the $[I_3^-]'$ interpretation that $[I_3^-]$ in these two equations may be replaced by $[I_3^-]'$.

* Inversion rate assumed to be much greater than $1/\tau_r$.

higher iodide contributes nothing to the relaxation.

The test to be applied to the calculations of Table III is the reasonableness of the $1/\tau_r$ values. The value estimated from hydrodynamic theory, as discussed earlier, is $1/\tau_r = 2.3 \times 10^{10} \text{ sec}^{-1}$ at 25° , with considerable uncertainty. This value is in severe disagreement (20 fold) with cases A, 2, (a) and B, 2, (a) and therefore it is concluded that the exchange process is not restricted to the weakly bound end iodine of an unsymmetrical I_3^- .

The hydrodynamic estimate of $1/\tau_r$ is about equally close to the derived values for the other two pairs of mechanisms for exchange, with no significant basis for favoring one set over the other.

Although only the data for the 0.1M and 1M I^- solutions at ionic strength 2.0 M have been used in the above interpretation, the values in Table I at 0.4 and 2.0 M I^- are reasonably consistent. The precise shape of the curves of Fig. 2 was not believed to be definitive in the fitting because of uncertainties about the amount of I_4^{2-} and its relaxation behavior. The point at 0.05M I^- , when placed on Fig. 1, lies above the other data, as would be expected from a sizeable activity coefficient correction to the rate of exchange at the much lower ionic strength.

At the 1M iodide point the I_4^{2-} concentration is calculated from equation (4) to be 0.184 times the I_3^- concentration; therefore, the correction for the presence of I_4^{2-} is not trivial. The assumption made for the second set of k_5 and $1/\tau_r$ values of Table III, that the I_4^{2-} does not contribute to the relaxation, seems unrealistic from the

following argument. Bonding considerations point to a linear structure for I_4^{2-} . A simple molecular orbital picture of a symmetrical, linear structure places a "p" electron deficiency of 1/2 electron on each iodine, leading to an overall quadrupole relaxation parameter which is 3/4 that of triiodide when averaged over the four and the three positions respectively. With a somewhat slower tumbling rate for I_4^{2-} , the net result is a predicted relaxation rate per I_4^{2-} roughly equal to that for an I_3^- in the relaxation controlled region. Therefore, one might expect the parameters from the interpretation based on $[I_3^-]$ to be closer to the actual situation.

It seems likely that the I_4^{2-} is an intermediate in the exchange process between I^- and I_3^- . If so, the mechanism consists of attack by the I^- on the end of the I_3^- , i.e., the second group of mechanisms in Table II. If I_3^- is symmetrical or inverts any asymmetry rapidly relative to relaxation, all three positions of I_3^- become available for relaxation in the relaxation controlled limit. Such a situation corresponds to cases B,1 and B,2,(b), respectively, of Table II. These would seem to be the most likely mechanisms. In either case the bimolecular rate constant k_5 is near, but within, the diffusion limit.

Very recently Turner, Flynn, Sutin and Beitz²³ have measured the formation and dissociation of triiodide by means of a laser temperature-jump apparatus. Their data show that the exchange of I^- with I_3^- by the mechanism of equation (1) is unimportant relative to that by equation (9) in the present study.

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FIGURE CAPTIONS

Figure 1: Variation of line broadening with triiodide concentration for 2.0 M iodide solutions at 27°C.

Figure 2: Plot of $1/k_1$ and $1/k_2$ (see Equation 6) versus the iodide concentration.

Figure 3: Temperature dependence of $[I^-]\delta/[I_3^-]_{app}$ for triiodide solutions: 0.4 M iodide $\circ$, 1.0 M iodide $\circ$, 2.0 M iodide Δ .

Figure 4: Temperature dependence of peak-to-peak line width of iodide ion in the absence of triiodide: 0.1 M KI $\circ$, 2.0 M $\circ$. The activation energies for the iodide line width are the same within experimental error for the 0.1 M and 2 M KI solutions. The slope is fixed by the experimental points and the line is drawn through the accurately known value of the linewidth at 27° C, i.e., $1.15 \pm .03$ gauss.

Figure 5: Temperature dependence of line broadening for a solution 0.05 M in iodide and 1.07×10^{-5} M in triiodide.

XBL 726-6419

Fig. 1

XBL 726-6420

Fig. 2

MU - 24423A

Fig. 3

MU-24540A

Fig. 4

MU-24421A

Fig. 5

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TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720