

with $\mu_i = \mu_{O_2}(1 + \alpha)$.

To first order

$$\Delta P = -\alpha\mu_{O_2}P_i^2 + \Delta n \frac{RT}{V} \quad (\text{A-7})$$

where $\mu_{O_2} = 6.07 \times 10^{-4} \text{ atm.}^{-1}$ at 25° and

$$\alpha = 3.21X(1 + 1.33X)$$

where X is the mole fraction of CO_2 in the final state.⁸ RT/V is a constant of the bomb.

The corrections to standard states in this paper were made using eq. A-4 and A-7. The energy of solution of CO_2 in the bomb liquid is negligible for our work for the liquid volumes present. The initial temperatures for the combustions were at 25.00° , the same as the reference temperature.

Iodine Complexes with Cyclohexanone and Related Compounds¹

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Studies were made of the ultraviolet and visible absorption spectra of iodine complexes with cyclohexanone and related compounds in Freon solution. Charge-transfer bands occur at 242 m μ for acetone, 249 m μ for 2-cyclohexenone, 233 m μ for cyclohexanol, and 253 m μ for both cyclopentanone and cyclohexanone complexes. Equilibrium constants, extinction coefficients, and enthalpies for these complexes are given. At higher concentrations of the ketones, a second type of complex with absorption maxima at 300 and 375 m μ dominates the spectra. Since its concentration varies as the square of the first complex concentration, it is thought to be a dimer complex. The dimer complexes have unusually high formation energies of about 20 kcal./mole.

I. Introduction

It is now generally believed that the noninert solvents for iodine which result in a color other than violet form charge-transfer complexes with iodine.³ More particularly, it has been suggested that oxygen-containing solvents form iodine complexes through the oxygen lone-pair electrons. Although ketones appear to form strong complexes, they have not been studied extensively, possibly because iodination is thought to occur easily.⁴ Iodination can usually be avoided or delayed by dilution in an inert solvent, by cooling, and by minimum exposure to light. Infrared studies of acetone and cyclohexanone in solution with iodine have demonstrated that a complex is formed and that the iodine molecule is bound to the keto oxygen.⁵

II. Experimental

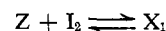
Measurements of the visible and ultraviolet absorption spectra were made with a Perkin-Elmer Type 202 spectrophotometer using 1- and 10-mm. absorption

cells. Temperature was held to within $\pm 0.2^\circ$ of a pre-set value in the range -15 to $+35^\circ$ by means of an automatic temperature control.

Reagent grade acetone, cyclohexanone, cyclohexanol, and cyclopentanone were used without further purification except drying with Drierite. Hexachloroacetone (m.p. -5°) was recrystallized from dichlorodifluoromethane; 2-cyclohexenone was purified by fractional distillation (b.p. 42° at 5 torr). Trichlorotrifluoroethane, a Freon (F-113) which boils at 47° , was selected because it is an inert solvent⁶ of fairly high solubilization, is readily available in pure form (Dupont), and is transparent sufficiently far in the ultraviolet (230 m μ).

III. Monomer Complex Formation

When acetone, cyclopentanone, cyclohexanone, or 2-cyclohexenone, and iodine are dissolved in an inert solvent, two absorption bands appear in addition to those present in iodine and ketone (Z) alone, as shown in Figures 1 and 2. These two bands are attributed to a 1:1 charge-transfer complex (X_1). The visible peak of



the complex at 465 m μ lies close to the normal visible I_2 band at 520 m μ (ϵ 870) and is due to a shift of the normal I_2 band.³ The ultraviolet peak at 230–260 m μ is identified as the charge-transfer band.

Because of the limited solubility of iodine in Freon ($\sim 10^{-2} M$), an excess of ketone was used to produce a measurable concentration of the complex. Only a small fraction of the ketone was found as a complex so that its concentration at all times was practically equal to the initial concentration. Thus, its ultraviolet absorption spectrum could be subtracted from the total spectrum.

Often an appreciable fraction of the iodine was bound in the complex. The free iodine can be measured spectrophotometrically if allowance is made for absorption of the complex which overlaps the free iodine band. A spectral subtraction procedure indicated a

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(2) Fellow of the USPHS Training Program at Roswell Park Memorial Institute.

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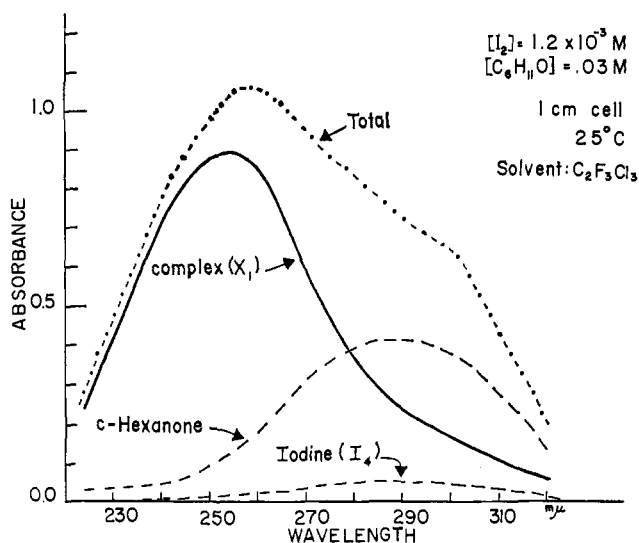


Figure 1. Ultraviolet absorption band of cyclohexanone-iodine complex. The cyclohexanone and iodine absorptions are subtracted from the total absorption to obtain the complex absorption.

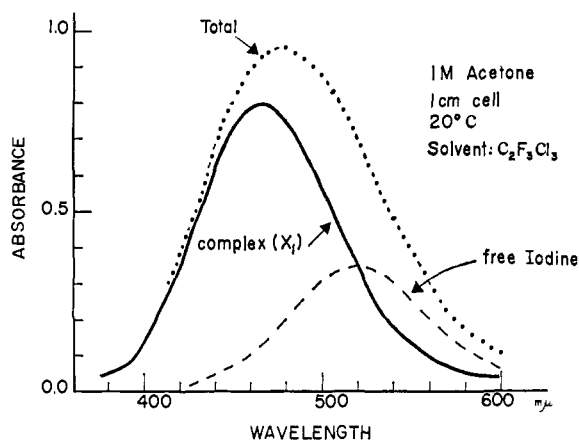
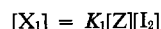


Figure 2. Visible absorption band of acetone-iodine complex. Solutions with various acetone concentrations but the same initial iodine concentration produce spectra which pass through an isobestic point at 495 $m\mu$. The visible bands of the other complexes are very similar.

1:1 formula complex was formed, following the relation



where $[X_1]$ is the (monomer) complex concentration and $[Z]$ is the ketone concentration. The equilibrium constant K_1 was obtained by a procedure which avoids the necessity of first splitting the spectra into components.³ Recognizing that the optical absorbance A , at any wave length where the ketones do not absorb, is $\epsilon(I_2)[I_2] + \epsilon(X_1)[X_1]$ for a 1-cm. path, it can be shown that $A_0/(A_0 - A)$ is a linear function of $1/[Z]$, where $\epsilon(I_2)$ and $\epsilon(X_1)$ are the extinction coefficients of the free iodine and the complex, respectively, and A_0 is the (free iodine) absorbance at $[Z] = 0$. The slope and intercept have the values given in Figure 3. From plots such as Figure 3, K_1 as well as $[I_2]$ and $\epsilon(X_1)$ as a function of λ can be obtained. Although not apparent from Figure 3, K_1 actually decreases at higher ketone concentrations.

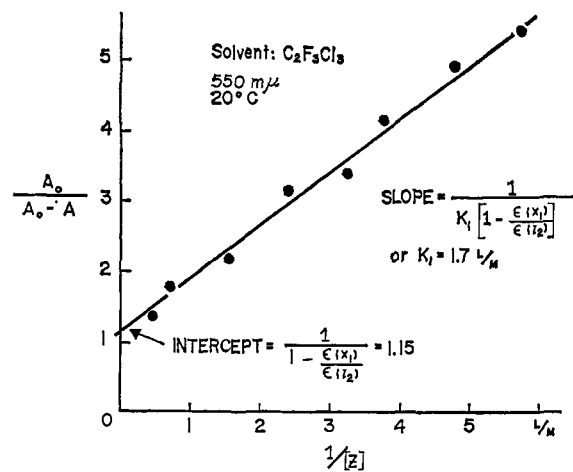


Figure 3. Reciprocal concentration plots for acetone-iodine solutions. The equilibrium constant (K_1) for complex formation is obtained from this plot.

As is often found, complex formation is favored by lowering the temperature. A plot of the equilibrium constant on a log scale as a function of reciprocal temperature resulted in a straight line and from its slope the enthalpy (ΔH_1) or formation energy was found.

A list of measured enthalpies, free energies ($\Delta F = -RT \ln K$), and entropies ($T\Delta S = \Delta H - \Delta F$) is given in Table I together with spectral data. Note that the spectra as well as the thermodynamic constants of the complexes are rather similar. Substantially lower values for K_1 were reported by Yamada and Kozima⁵ (0.28 and 0.56 l./mole) for acetone and cyclohexanone complexes, respectively, at 30° in CS_2 .

An iodine complex with hexachloroacetone was found ($\lambda_{max} 255 \pm 10 m\mu$) but was weak ($K_1 \approx 0.01$ l./mole). This shows that the enol form is not necessary for complex formation and supports the assumption that the oxygen lone-pair electrons are involved. On the other hand, it is an oversimplification to think of the charge-transfer bond in ketones as involving only isolated lone-pair electrons. An indication of valence electron involvement is the effect of halogen substitution in reducing the free energy. Hexachloroacetone is a stronger Lewis acid than acetone, and as such is a poor electron donor. Thus, only weak complexes with iodine would be expected. Hexafluoroacetone is an even stronger Lewis acid and, as expected, no iodine complex was observed ($K_1 < 0.01$ l./mole).

IV. Dimer Complex Formation

At higher concentrations, a second type of complex is formed which, it will be argued, is a dimer of the complex already described: $2X_1 \rightleftharpoons X_2$. Once initiated, the dimer complex is in equilibrium with the ketone and iodine (as well as with the monomer complex X_1). However, spontaneous initiation often occurs very slowly especially in cooler, less concentrated solutions. A small amount of dimer already formed would initiate a freshly prepared solution. Dimer formation, as identified by the appearance of the absorption band given in Figure 4, may not occur for many hours after the iodine solution is mixed. But after the dimer begins to appear, its concentration relatively quickly approaches a stable value. To show that equilibrium is

Table I. Thermodynamic Constants and Spectra Maxima for Monomer Iodine Complexes

Compound	λ_{\max} , m μ	Log ϵ_{\max}	K_1 (20°), l./mole	$-\Delta F$, ^a kcal./mole	$-\Delta H$, ^a kcal./mole	$-\Delta S$, ^a e.u.
Acetone	242	4.05	1.7	1.6	5.8	14
	465	2.95				
Cyclopentanone	253	3.99	2.3	1.8	4.7	10
	465	3.00				
Cyclohexanone	253	3.99	2.4	1.8	6.1	15
	465	3.00				
Cyclohexenone	249	4.25	3.2	2.0	5.4	11
	465	2.95				
Cyclohexanol	233	4.02	2.2	1.7
	453	3.05				
Prob. error	± 5	± 0.05	$\pm 15\%$	± 0.2	± 0.5	± 2

^a Calculated in terms of mole fraction in Freon.

Table II. Thermodynamic Constants and Spectra Maxima for Dimer Iodine Complexes

Compound	λ_{\max} , m μ	Log ϵ_{\max}	K_2 (20°), ^b l./mole	$-\Delta F$, ^a kcal./mole	$-\Delta H$, ^a kcal./mole	$-\Delta S$, ^a e.u.
Acetone	~ 290	4.4	90	3.9	21	57
	370	4.50 ± 0.15				
Cyclopentanone	295	4.4	850	5.2	16	37
	375	4.4				
Cyclohexanone	300	4.4	1000	5.3	20	50
	375	4.4				
Cyclohexenone ^c	~ 300	...	(~ 100)	(~ 4)	(~ 20)	(~ 50)
	380					
Prob. error	± 15	± 0.4	$\pm 50\%$	± 0.3	± 4	± 10

^a Calculated in terms of mole fraction in Freon. ^b Calculated assuming $\epsilon(X_2) = 3.0 \times 10^4$ at 375 m μ . ^c Iodates rapidly.

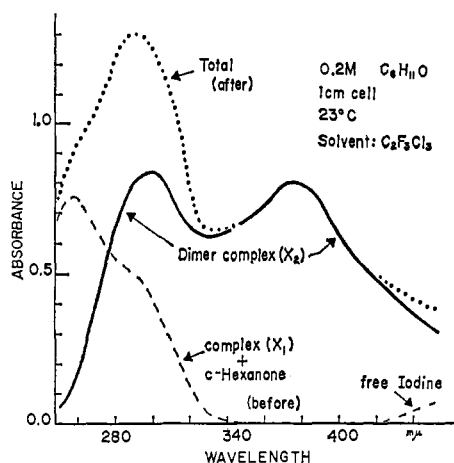


Figure 4. Absorption spectra of cyclohexanone-iodine dimer complex. The dimer spectra were obtained by measuring the change in absorption before and after the slow formation of the dimer in solution.

achieved, a solution can be prepared (*e.g.*, by dilution) such that the dimer concentration is temporarily above its equilibrium value. In this case, the dimer decomposes until it reaches the same value as is obtained by the approach from lower concentration.

The dimer complex concentration at equilibrium was found to increase with the square of the monomer complex concentration $[X_1]$, and therefore with the square of both the ketone concentration $[Z]$ and the iodine concentration $[I_2]$ according to the equation (see Figure 5)

$$[X_2] = K_2[X_1]^2 = K_2K_1^2[Z]^2[I_2]^2$$

In order to obtain $\epsilon(X_2)$, the disappearance of free iodine during the initial formation of the dimer was

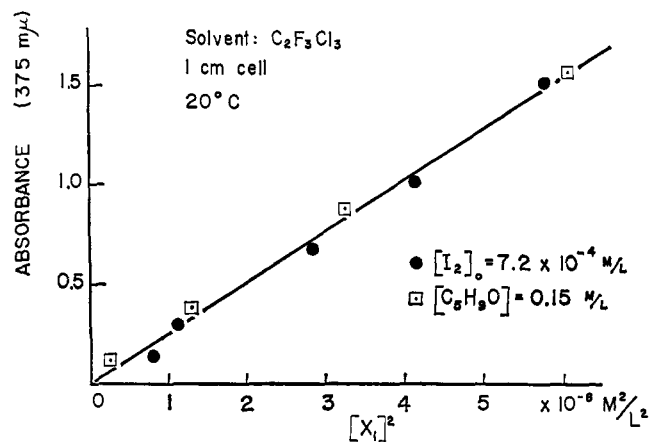


Figure 5. Graph showing the dependence of dimer concentration on the square of monomer concentration for the cyclopentanone-iodine complex. Two runs are shown, one with constant cyclopentanone concentration, the other with the same initial iodine concentration.

measured. Unfortunately, the dimer absorption strongly overlaps the single complex and free iodine absorptions at all wave lengths, resulting in a large uncertainty in the determination of $\epsilon(X_2)$. The dimer concentration was found to have a surprisingly strong temperature dependence, a factor of two for a 5° change. Correspondingly, ΔH_2 and ΔS_2 , the enthalpy and entropy for the formation of the dimer from the single complex, are high (Table II).

At higher concentrations, the cyclohexanol-iodine complex spectrum was somewhat similar to that of the dimers. However, the absorption was much weaker and equilibrium was not demonstrated. Perhaps im-

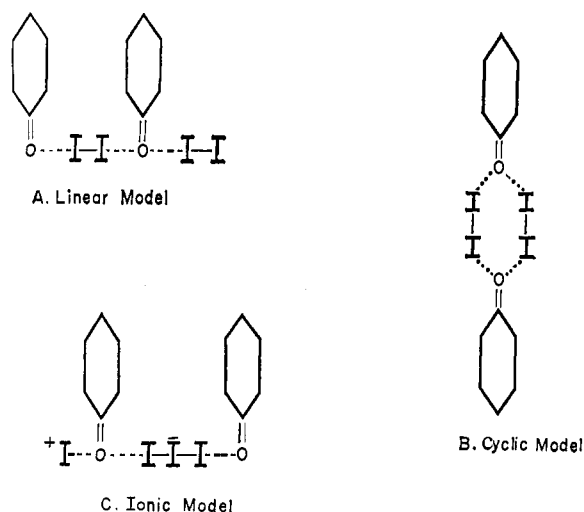


Figure 6. Postulated dimer structures. Additional structures involving the enol form are possible.

purity reactions give rise to the observed spectra in this case.^{7,8}

If a vessel containing more than 10^{-5} to 10^{-4} *M* of the dimer complex is allowed to stand, a yellow film (λ_{\max} 390 $m\mu$) may form and an oily liquid precipitates. Film formation inside the absorption cell was avoided in quantitative determination of the dimer complex absorption in solution. The precipitate appears to be a complex since it rapidly redissolves in Freon where it largely breaks up into free ketone and iodine.

The precipitate also readily dissolves in water, resulting in a spectrum very similar to that of I_3^- (and I_2) in water.⁹ Water extractions of acetone-iodine complex from Freon solutions containing the dimer display a similar spectrum except that much more acetone is present. It is suspected that the ionic form of the single "inner" complex, $(CH_3)_2C=OI^+I_3^-$, and not HI_3 , is present in water solution (see section VI).

V. Arguments Against Iodination

The spectral changes during the complex formation are rather similar to that expected for iodination. It is known that α -iodo ketones absorb strongly at about 250 $m\mu$. Since HI would be released, it could react with I_2 to form HI_3 which is known⁹ to absorb strongly at about 355 and 285 $m\mu$. Indeed, if a solution containing the cyclohexanone complex is allowed to stand in the presence of light at room temperature, the free iodine absorption (as well as the 375- $m\mu$ absorption) disappears in a few days and a colorless crystalline precipitate, probably α -iodocyclohexanone, appears. However, little iodination of the saturated ketones reported here occurs if the solutions are kept cool and away from strong light. Iodination of 2-cyclohexenone proceeded at an appreciable rate under all conditions and the results on this compound are therefore less certain.

It is fairly certain that the 240–255- $m\mu$ absorption is not due to an iodo ketone since the extinction coefficient of the iodo ketones is more than an order of magnitude

lower than that of the monomer complex (X_1). Further, the 465- $m\mu$ part of the complex absorption spectra is not found with iodo ketones.¹⁰

The reversible nature of the substance absorbing at 375 $m\mu$ upon dilution or temperature change strongly indicates it is not a product of iodination. This is particularly true because of the dependence on the square of the iodine and ketone concentrations. Since the free iodine present at any time can be determined photometrically, the iodine bound or reacted is known. It was found that, except for 2-cyclohexenone, the iodine not accounted for and thus which might have reacted to form HI was less than 10% of the iodine bound or 1% of the total iodine present (provided no yellow film had formed).

Benesi and Hildebrand⁴ have investigated acetone-iodine complexes. They interpret the 365–375- $m\mu$ absorption as due to HI_3 , a result of iodination. It is felt that the interpretation given here is consistent with their experimental observation and that they did not prove that HI_3 was actually present. The high electrical conductivity they observed in solution does, however, indicate that an ionic complex is formed.

VI. Postulated Dimer Structures

While the exact nature of the dimer complex is not clear, several structures are postulated. The first of the postulated structures, the linear model given in Figure 6A, is suggested by the structure determination of a bromine-acetone complex crystal reported by Hassel and Stromme.¹¹ They found that Br_2 molecules are situated midway between oxygen atoms, forming a long chain. The coordination of two iodine molecules to an oxygen atom is possible since two lone-pair electrons are available on the oxygen, allowing two (n, σ) charge-transfer bonds. It would be expected that chains longer than the dimer shown in Figure 6A would also form.

A variation of this structure is shown in Figure 6B. It is a more symmetrical structure and would explain the predominant dimer formation. Since there are four charge-transfer bonds, the formation energy per bond will be $(2\Delta H_1 + \Delta H_2)/4$. For the cyclohexanone complex this quantity (8 kcal./mole) is at least comparable to the value for the first bond formed (6.1 kcal./mole). The formation energy per bond for a cyclohexanone complex linear dimer (Figure 6A) would be $(2\Delta H_1 + \Delta H_2) \approx 11$ kcal./mole, a value too high to be readily acceptable.

The third and most likely structure, the ionic model, is given in Figure 6C. It is based on the idea that the complex can change from an "outer" to an "inner" complex. Reid and Mulliken¹² gave evidence that the pyridine-iodine complex exhibits this transformation. An "outer" complex should be easily ionized so that I_3^- would be formed, although still bound in the complex. This model has the advantage of explaining why the dimer spectrum is so similar to the spectrum¹³ of I_3^- . The atomic rearrangement to form an inner complex could account for the observed large heat of for-

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mation. At higher ketone concentrations, the solution is more polar and would favor the formation of an ionic complex. An ionic nature is also suggested by the water solubility and by the large entropy change. Large entropy changes usually occur during formation of ionic compounds in solvents which are not highly polar.

While the iodine molecules in Figure 6 are drawn to suggest bonding to the lone-pair electrons of the keto

oxygen, it is likely that π -electron bonding is also involved. Other structures could be drawn with the dimer complex in the enol form. There are, in fact, a fairly large number of structures possible. Certainly there are enough possibilities to make plausible the assumption of dimer and even polymer charge-transfer complex formation.

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The Photoproduction and Recombination of Bromine Atoms in the Liquid Phase

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Contribution from the Institute of Physical Chemistry, University of Uppsala, Uppsala, Sweden. Received April 15, 1965

The photoproduction and recombination of bromine atoms in carbon tetrachloride has been studied at room temperature by flash spectrophotometric techniques. The primary quantum yield of dissociation ($\phi = 0.22$) is ca. 100 times as great as that deduced previously by indirect means, but is only slightly greater than that for iodine under comparable conditions, in agreement with the assumption that the solvent behaves as a continuous medium. The second-order rate constant is $k = 1 \times 10^{10} \text{ l. mole}^{-1} \text{ sec.}^{-1}$, where $d[I]/dt = 2\phi I_a - 2k[I]^2$, in correspondence with a diffusion-controlled recombination process involving small diffusive displacements.

Introduction

The primary quantum yields of photoproduction and rates of recombination of iodine atoms in inert solvents have been determined by several techniques, including flash photolysis²⁻⁴ and a combined rotating sector⁵-steady-state illumination,⁶ or rotating sector-allyl iodide atom scavenger method.^{7,8} Results obtained by the various methods are in quite satisfactory agreement and have been used in combination with photochemical space intermittency effect results to measure iodine atom diffusion coefficients^{9,9a} and to develop a theory of solution photodissociation based on the solvent as a continuous medium.¹⁰

The primary quantum yield of photodissociation of molecular bromine in carbon tetrachloride has been deduced indirectly from a comparison of the thermal and photochemical exchange reactions between bromine and bromotrichloromethane.¹¹ Assuming the same reaction mechanisms and rate constants (except for the initial step), and that the constant for the equilibrium between bromine atoms and bromine molecules is the same in the gas and liquid phases, the quantum yield equals 0.0025 at 50°. This result is surprisingly low in comparison to that for iodine (0.14 at 25° 0.21 at 38°),⁷ as theoretically the primary quantum yield for bromine should be somewhat *greater* as a result of the smaller atomic diameter and the greater excess energy (following dissociation) of the bromine atoms.

In attempting to determine the recombination of bromine atoms in carbon tetrachloride by measuring the decrease in steady-state molecular concentration upon illumination by a relatively strong continuous light source, Rabinowitch and Wood actually observed a very small *increase* in absorption in the visible region.^{6,12} A similar but stronger effect was observed for iodine in benzene, methanol, and water, and in the case of benzene was attributed either to the destruction of a benzene-iodine complex by light or to the formation during illumination of a new complex involving iodine atoms.¹² More recent studies of iodine-benzene solutions by flash techniques have shown the same increase in absorption^{13,14} and have led to the conclusion that a charge-transfer complex is formed between the benzene molecule (donor) and iodine atom (acceptor) species. Although carbon tetrachloride does serve as an acceptor in some charge-transfer interactions,¹⁵ the complexes are in general quite weak, and it is very doubtful that the increased absorption ob-

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(9a) NOTE ADDED IN PROOF. R. M. Noyes (private communication; *J. Phys. Chem.*, to be published) has revised downward the iodine atom diffusion coefficients by approximately a factor of two from those given in ref. 9.

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