with the photolysis radiation transmitted by the filter No. 7380. This implied absence of the ethylene precursor is accompanied by loss of the absorptions reported at 4182, 3968 and 3050–3300 Å. Similar behavior was found for deuterated diazomethane since the visible–ultraviolet absorptions found in Experiment 4 were absent in Experiment 5 (in which the filter No. 7380 was used). We are led to some important conclusions concerning the observed electronic transitions:

(a) *The substance which causes the infrared absorptions of type C is not the cause of the visible–ultraviolet absorptions of Experiment 1.* The infrared bands are obtained with light transmitted by filter No. 7380; the visible–ultraviolet absorptions are not.

(b) *The ethylene precursor, presumably methylene, could be the species responsible for one or more of the visible–ultraviolet absorptions, 4182, 3968 and 3050–3300 Å.*

Conclusions

These results may provide significant aid in the search for absorptions of methylene by more conventional spectroscopic means. Still the identification of methylene as the cause of any or all of these absorptions is quite tentative and a detailed interpretation seems to be unwarranted here. There are, of course, obvious and important implications of the frequencies observed for the normal and deuterated species if methylene is indeed responsible.[11]

Acknowledgments.—Grateful appreciation is expressed for fellowship aid (to T.D.G.) from Texaco Company and for research support by the American Petroleum Institute Research Project 54 and the United States Air Force through the AFOSR of the Air Research and Development Command under Contract No. 49(638)-1. We also wish to thank Drs. G. Herzberg and J. Shoosmith, who kindly sent us a preprint of their note on methylene,[4] and to acknowledge helpful and informative communications from Professor G. W. Robinson.[12]

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[11] These implications are explored in detail in the Doctoral Dissertation of Theodore D. Goldfarb, University of California, Berkeley, 1959.

[12] During the preparation of this manuscript, Professor Robinson kindly forwarded to us a copy of his manuscript with Dr. M. McCarty, Jr. on "The Production and Subsequent Photolysis of Transient Products from the Photodecomposition of Diazomethane at 4.2°K." A comparison to the work presented here emphasizes the interdependence of the two studies. The following specific comments are stimulated by our perusal of the Robinson–McCarty manuscript.

(a) If methylene is isolated, whether in solid krypton or nitrogen, it is surely expected that it will act as an ethylene precursor when diffusion occurs. Hence our failure to observe the growth of ethylene when a filter No. 7380 is used probably indicates the absence of a large amount of methylene under these conditions. This conclusion is not dependent upon the correctness of our conviction that methylene is the ethylene precursor in the present work.

(b) Since Robinson and McCarty indicate a correspondence between their observations in the region near 2600 Å. and those of DeMore and Davidson,[10] we feel the results and discussion of our Experiment 2 pertain to the work of Robinson and McCarty.

(c) The comments of Robinson and McCarty on the different photolytic behavior of deuterated diazomethane are of particular interest to us. We have accumulated a substantial amount of infrared evidence which is in agreement with their conclusion and which is, perhaps, of crucial importance in their interpretations. We have observed that bands analogous to the Class C infrared absorptions are *not* produced from deuterated diazomethane, though the ethylene precursor *is* still produced. This substantiates their conclusion that photolysis of CD_2N_2 differs from that of CH_2N_2 and suggests that the substance responsible for the Class C bands[1] could be important in the studies of Robinson and McCarty.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE CHANDLER LABORATORY OF COLUMBIA UNIVERSITY AND FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF OREGON]

The Effect of Viscosity on the Quantum Yield for Iodine Dissociation

BY DAVID BOOTH AND RICHARD M. NOYES[1]

RECEIVED AUGUST 3, 1959

The quantum yields for dissociation of iodine by the 4358 Å. mercury line have been measured at 25° in a number of hydrocarbon solvents. Data now available for hydrocarbon solvents cover a range of 10^3 in viscosity and two chlorocarbon solvents also have been studied. Quantum yields in the least viscous solvents are not greatly different from those predicted by hydrodynamic theories if dissociating iodine atoms are slowed by viscous drag and then diffuse at random in a structureless viscous continuum. However, quantum yields in hydrocarbons are somewhat greater than the absolute values predicted by the viscous continuum model, while quantum yields in chlorocarbons are less; detailed description of the observations must invoke solvent–solute interactions and must recognize that viscosity is not a sufficient parameter to account for all of the effects of changing solvent. In viscous hydrocarbon solvents, the observed quantum yields are many times those predicted by the viscous continuum model. These quantum yields also approach a limiting value that is not reduced by further increase in viscosity, while the most logical method of applying the viscous continuum model predicts that the quantum yields approach zero with indefinite increase in viscosity. The results suggest ways in which molecular structure of solvent must be introduced in order to describe these systems fully.

Introduction

When a molecule of iodine is dissociated photochemically in solution, the separating atoms are slowed to thermal velocities while the distances traversed are still comparable to molecular dimensions. The atoms then diffuse at random and may either recombine with each other in a very short time or else diffuse apart and subsequently undergo other reactions.

In solvents of low viscosity, the initial separation will be greater and there will be a greater quantum yield for the production of atoms that become permanently separated from their original partners. Although this qualitative picture is clear and in agreement with experiment, a quantitative theory of quantum yields has not been developed at the

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molecular level. Also, the existing measurements of quantum yield are too few to permit discrimination among molecular models that might be adopted for theoretical treatment.

This paper reports measurements of quantum yield for iodine dissociation at constant wave length in five hydrocarbon solvents of widely different viscosities. Since these solvents were supposedly identical in chemical properties but differed in viscosity and molecular weight, the data provide the sort of information of value for testing mathematical theories.

The method of measurement was the allyl iodide scavenging technique developed by Lampe and Noyes.[2] Any iodine atoms that escape their original partners react with allyl iodide to form iodine molecules and allyl radicals. The allyl radicals then react with atmospheric oxygen to form comparatively inert radicals that ultimately react to form stable products not containing iodine. Therefore, the rate of photochemical production of molecular iodine in an air saturated solution of allyl iodide becomes a direct measure of the rate of photochemical production of free iodine atoms. These atoms come from dissociation of both allyl iodide and molecular iodine but the contributions from the two dissociations can be separated by measuring rates at different concentrations of the species involved.

Experimental

Materials.—The five solvents used in this study were refined petroleum "white oils" kindly supplied by Dr. F. W. Lampe of the Humble Oil and Refining Company. The densities were measured by direct weighing, and the average molecular weights were determined commercially by freezing point depression in camphor. The viscosities were measured with capillary viscometers calibrated against sucrose solutions and glycerol. None of the solvents contained impurities reacting with more than about 10^{-6} mole/l. of iodine. Absorption spectra in the region 3000–3600 Å. gave no evidence of tendency to form complexes with molecular iodine.

Commercial allyl iodide was purified with aqueous sulfite, dried and vacuum distilled as described by Sibbett and Noyes.[3] The freshly distilled material was dissolved in solvent and stored at −5°. Gas chromatography indicated a small impurity peak with area about 0.4% that of the main peak.

Resublimed reagent-grade iodine was used without further purification.

All solvents were as transparent as water at 4360 and 5250 Å. Extinction coefficients, E, defined by the equations

$$D \equiv \log (I_0/I) = EcL \qquad (1)$$

were measured for both allyl iodide and iodine at 4360 and 5250 Å. in each solvent. Absorption by allyl iodide at the latter wave length was always negligible. The properties of these solvents and those studied previously[2] are summarized in Table I. The uncertainties in values reported for the first time are twice standard deviations of individual measurements.

Apparatus and Procedure.—Solutions of iodine and allyl iodide in each solvent were thermostated at 25° in optical cells and illuminated with the 4358 Å. line isolated from a thermostated AH-4 mercury arc. For the less viscous solvents, the line was isolated by glass filters that transmitted only a small fraction even of the desired line. For the more viscous solvents where the quantum yields were lower, it was necessary to use a filter solution of crystal violet and 9,10-dibromoanthracene in toluene–ethanol.[4] Spectrophotometric measurements demonstrated that this filter solution transmitted less than 1% of the light from the other principal lines in the mercury spectrum. The arc was monitored with a photo cell, and the absolute incident intensity, I_0, was measured with the ferrioxalate actinometer of Parker[5] on the assumption that $\phi_{4358} = 1.11$.

TABLE I

PROPERTIES OF SOLVENTS

Solvent	η, poise	Mol. wt.	E_{I_2} (4360 Å.)	E_{AI} (4360 Å.) (E in l./mole cm.)	E_{I_2} (5250 Å.)
Hexane[a]	0.0029	86	46 ± 1	0.036 ± 0.002	881 ± 4
Bayol D	.017	333	87 ± 7	.044 ± .004	940 ± 11
NF 65	.54	409	68 ± 5	.045 ± .004	936 ± 10
NF 95	.8	624	77 ± 4	.051 ± .004	945 ± 7
USP 180	1.8	478	82 ± 3	.045 ± .004	945 ± 2
USP 335	3.8	458	87 ± 2	.045 ± .004	918 ± 26
CCl_4[a]	0.0092	154	67 ± 1	.038 ± .007	920 ± 4
C_4Cl_6[a]	0.030	261	57 ± 7	.062 ± .011	936 ± 10

[a] Data from ref. 2

The illumination was interrupted periodically and the concentration of iodine was measured spectrophotometrically at 5250 Å. The data were used to calculate R, defined by

$$R = \frac{2.30D}{1 - e^{-2.30D}}\,\mathrm{d}[\mathrm{I_2}]/\mathrm{d}t = \phi_{\mathrm{I_2}}\alpha_{\mathrm{I_2}}I_0[\mathrm{I_2}] + \phi_{\mathrm{AI}}\,\alpha_{\mathrm{AI}}\,I_0[\mathrm{AI}] \qquad (2)$$

where $\alpha_{I_2} = 2.303\ E_{I_2}$ and ϕ's are quantum yields for dissociation of iodine and allyl iodide. The derivation of these equations has been discussed previously.[2]

Results

R values were measured in each solvent for a series of solutions containing the same allyl iodide concentration but different initial concentrations of iodine, and least squares procedures were applied to equation 2 to calculate quantum yields for the dissociation of both species. The R values for different runs are presented in Table II. The quantum yields for allyl iodide and iodine dissociation are presented in Table III along with some calculated quantities whose significance is discussed later. The uncertainties reported in new values are twice standard deviations and represent maximum reasonable errors.

Discussion

Development of Theory.—The data demonstrate that increasing viscosity of hydrocarbon solvents can profoundly depress quantum yields for dissociation into radicals. The data for allyl iodide dissociation do not show any consistency with viscosity. For the three very viscous solvents NF 95, USP 180 and USP 335, the 4358 Å. line was isolated with a shorter length of filtering solution than for the less viscous NF 65. Although the filtering solution would pass only a very small fraction of the intense mercury line at 3650 Å., the allyl iodide undoubtedly absorbs much more strongly in this region than at 4358 Å. Also, the more energetic quantum is more efficient at causing dissociation and a small contamination of 3650 Å. in the beam could greatly increase the ap-

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(2) F. W. Lampe and R. M. Noyes, THIS JOURNAL, **76**, 2140 (1954).

(3) D. J. Sibbett and R. M. Noyes, *ibid.*, **75**, 761 (1953).

(4) A. Burawoy and A. G. Roach, *Nature*, **181**, 762 (1958).

(5) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.* (*London*), **235***A*, 518 (1956).

parent values of ϕ_{AI}. We therefore tend to discredit the quantum yields for allyl iodide reported in the more viscous solvents.

TABLE II

PHOTOCHEMICAL IODINE PRODUCTION AT 25°

$I_0 \times 10^{10}$, einstein/cm.^{2} sec.	[AI] mole/l.	Initial $[I_2] \times 10^5$ mole/l.	$R \times 10^{10}$, mole/l. sec.
	Bayol D		
1.63 ± 0.08	0.140	5.57	7.60
		9.46	10.3
		11.01	11.3
		12.88	12.1
		14.94	12.9
		15.75	14.1
		17.19	14.6
	NF 65		
2.58 ± .08	.132	5.53	2.35
		7.48	2.58
		10.45	3.75
		11.67	4.36
		14.84	5.29
		16.46	5.92
	NF 95		
7.91 ± .48	.143	5.44	6.16
		7.19	7.12
		7.58	7.71
		9.38	8.00
		10.95	9.79
		14.51	12.25
	USP 180		
10.0 ± .5	.119	5.54	5.30
		7.20	6.07
		8.28	7.08
		9.08	7.23
		10.05	8.54
		11.64	9.53
		13.04	10.38
		14.86	11.80
	USP 335		
10.0 ± .5	.146	5.01	5.65
		6.67	6.29
		8.54	8.41
		10.48	9.63
		12.42	10.54
		14.05	12.20

TABLE III

QUANTUM YIELDS AND DERIVED QUANTITIES

Solvent	ϕ_{AI}	ϕ_{I_2}	ϕ_{I_2} (calcd.) Method I	ϕ_{I_2} (calcd.) Method II
Hexane[a]	0.54 ± 0.04	0.66 ± 0.04	0.52	0.47
Bayol D	.20 ± .04	.18 ± .025	.145	.155
NF 65	.006 ± .011	.086 ± .010	.0052	.040
NF 95	.018 ± .008	.048 ± .008	.0035	.038
USP 180	.009 ± .005	.038 ± .004	.0016	.037
USP 335	.013 ± .006	.036 ± .005	.0007	.036
CCl_4[a]	.14 ± .03	.14 ± .01	.242	.235
C_4Cl_6[a]	.049 ± .008	.075 ± .009	.086	.107

[a] Data from ref. 2.

Fortunately, elementary iodine does not absorb strongly at 3650 Å. and the reported quantum yields would not be seriously affected by slight contamination in the beam used. Moreover, iodine dissociates into two identical atoms having virtually spherical symmetry, while allyl iodide dissociates into more complicated fragments. The subsequent discussion will be confined to the iodine quantum yields because of their greater probable accuracy and their greater theoretical tractability.

The data were obtained in order to permit experimental tests of predictions by detailed theories for these processes. The quantum absorbed by an iodine molecule contains much more energy than is needed to break the chemical bond and this excess appears as an initial kinetic energy of the dissociated atoms moving in opposite directions. Interactions with solvent slow the atoms to normal thermal velocities and they then diffuse at random and may eventually recombine with each other. If the solvent is treated mathematically as though it were a homogeneous viscous continuum rather than as a collection of discrete molecules, the probability of subsequent recombination of the dissociated atoms is inversely proportional to the separation attained before they start moving at random, and the models we have developed previously[6] predict that

$$1 - \phi = \beta' \rho / r_0 \qquad (3)$$

where β' is the probability a pair of atoms separating with normal thermal energies would recombine, ρ is the separation of the centers when contact between atoms is assured, and r_0 is the separation of the centers when the photochemically produced atoms begin to diffuse at random.

A macroscopic body moving in a fluid is subjected to a frictional drag proportional to the viscosity of the medium and for any particular initial velocity the body will be brought to rest in a distance inversely proportional to this viscosity. As a result of a suggestion by Professor F. C. Collins of the Polytechnic Institute of Brooklyn, we have applied this same model to the atoms separating from a dissociation. Each atom loses its excess kinetic energy in a distance $(r_0 - \rho)/2$ and for constant energy of the absorbed quantum this distance should be inversely proportional to η. Then equation 3 can be rewritten as

$$1 - \phi = \frac{\beta'}{1 + A/\eta} \qquad (4)$$

where A is constant at a particular wave length of light but independent of the solvent.

We have carried this argument further in another publication[7] and have shown that if the frictional force per unit area on an atom is the same as that on a macroscopic sphere, and if ρ is equal to the diameter of an atom, then

$$A = \frac{2\sqrt{m(h\nu - \epsilon)}}{3\pi\rho^2} \qquad (5)$$

where m is the mass of an atom and ϵ is the strength

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[6] R. M. Noyes, THIS JOURNAL, **78**, 5486 (1956).

[7] R. M. Noyes, *Z. Elektrochem.*, to be published.

of the bond that is broken. If the diameter of an iodine atom is 4.30 Å. and if the strength of the bond is 35.5 kcal./mole, application of equation 5 gives

$$A = 0.00241 \text{ g./cm. sec. (poise)} \qquad (6)$$

for light of 4358 Å.

Comparison with Experiment.—The equations developed above come very close to permitting a direct comparison of experimental results with a theory that uses only parameters capable of independent measurement. The only other parameter is β' and it will be close to but slightly less than unity. For the less viscous solvents, the values of ϕ calculated from the above equations are not at all sensitive to the value chosen for β' but the values for the very viscous solvents are highly sensitive to the value chosen. We have therefore selected two rather different methods of estimating β' and have used them to calculate the quantum yields to be expected for iodine dissociation in these solvents.

Method I: One possible method is to try to estimate β' from first principles by the same type of argument used above. If two particles separate at thermal velocities, the average kinetic energy of the center of mass of the system is $^3/_2kT$, and the average kinetic energy associated with separation of the particles is also $^3/_2kT$. The quantity A_t is defined by

$$A_t = \frac{\sqrt{6mkT}}{3\pi\rho^2} \qquad (7)$$

Here A_t differs from A only in that $^3/_2kT$ has been substituted for $h\nu - \epsilon$. At 25°, $A_t = 0.000415$ poise.

If iodine atoms are sure to combine if they encounter each other, the same argument used to obtain equation 4 leads to

$$\beta' = \frac{1}{1 + A_t/\eta} \qquad (8)$$

If this equation is applied to the solvents of the present study, $\beta' = 0.875$ for hexane and 0.9560 for carbon tetrachloride. The other values are still closer to unity and reach 0.99989 for USP 335. Some additional measurements of the effect of wave length on quantum yield[8] suggest that these calculated values of β' are surprisingly close to those pertaining in at least the most fluid of the present solvents.

The penultimate column of Table III contains quantum yields for iodine dissociation in these solvents calculated from equation 4 with β' values calculated from equation 8.

Method II: The second method we have adopted is to calculate β' for the most viscous solvent studied by assuming that equation 4 is valid for this solvent and that the value of A is given by equation 6. This calculation gives $\beta' = 0.9646$. We have then assumed that the same value of β' obtains in all of the other solvents and have calculated the quantum yields accordingly. The results are presented in the ultimate column of Table III.

Critique.—The theory developed above gives surprisingly good agreement with experiment when applied to solvents of low viscosity. However, detailed comparison reveals three systematic discrepancies which illustrate the types of refinements needed for further progress. These three discrepancies and their implications are discussed below.

(1) *The quantum yields in hydrocarbon solvents are invariably higher than predicted for the observed viscosity and the quantum yields in chlorinated solvents are lower than the predicted values.* This discrepancy demonstrates that viscosity is not a sufficient criterion to classify the properties of a solvent. Since the chemical nature of the solvent can even influence the sign of the difference between measured and predicted quantum yields, subsequent developments must recognize specific influences of intermolecular potentials.

It would be anticipated that the diffusion coefficient of iodine atoms in a solvent would be a better criterion for predicting quantum yield than is viscosity. Diffusion coefficients of iodine atoms are not known but they are presumably proportional to the rate constants for iodine atom recombination in different solvents. These rate constants have been measured already for three of the solvents with known quantum yields.[9] The rate constants in different solvents change by *smaller* percentages than the viscosities. In order to resolve the discrepancy of the present paper between quantum yields in hexane and in chlorinated solvents, it is necessary to invoke an effect that varies even *more* rapidly than the viscosities do.

A referee has suggested another interpretation to account for the discrepancy. If an iodine atom is slowed by elastic collisions with solvent molecules, it can lose more of its energy in a single collision the more nearly the effective mass of the colliding solvent molecule approximates that of the iodine atom. If only small segments of large molecules are effective in these collisions, chlorocarbons should be more effective than hydrocarbons at reducing quantum yields.

(2) *Increasing viscosity of hydrocarbon solvent does not depress the quantum yield as much as is predicted.* Although the calculated and observed quantum yields are quite comparable in hexane (0.0029 poise), the quantum yield in USP 335 (3.8 poise) is about fifty times the value calculated by Method I. If an empirical correction is used in Method II to adjust theory and experiment for USP 335, the quantum yield observed in NF 65 (0.5 poise) is still over twice the calculated value. Regardless of the method of calculation used, the theory predicts either that the quantum yield should be very small for all viscosities greater than a few tenths of a poise or else that quantum yields should be almost constant for these higher viscosity solvents. Although the data do suggest a limiting quantum yield as discussed below, the viscosities needed to approach it are almost ten times those predicted by the theory.

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[8] L. M. Meadows and R. M. Noyes, THIS JOURNAL, **82**, 1872 (1960).

[9] H. Rosman and R. M. Noyes, *ibid.*, **80**, 2410 (1958).

These observations again emphasize that viscosity is not a sufficient criterion for predicting the behavior of molecules. Viscosity depends on the interaction of solvent molecules with each other and the very viscous solvents contain large molecules that interfere with each other's motions. The iodine atoms are much smaller than the solvent molecules. Viscosity should vary approximately as the square of molecular complexity but the ability of an atom to move through the medium should depend more nearly on the first power of this complexity. Although these ideas are very crudely expressed, they rationalize the observation that increasing viscosity increases the factor by which the observed quantum yield exceeds the value calculated by Method I.

(3) *The quantum yields in viscous solvents approach a limiting value that is not reduced by further increases in viscosity.* Although Method II can be made to reproduce this effect, it does so only by means of an *ad hoc* assumption that is inconsistent with the idea of a viscous solvent continuum as used in the rest of the derivation; in fact, the assumption of Method II is tantamount to postulating that the observed effect does exist!

If quantum yields in USP 335 were measured at longer wave lengths, Method I predicts that the value for red light should fall to well below 0.01, while Method II predicts that it should remain about. 0.036. Our experience with other solvents[8] makes us feel that the assumption of Method II would be rejected if this experimental test were performed.

If the assumption of Method II can indeed be rejected, the observed limiting quantum yield is in direct violation of the predictions of the theory based on the solvent as a viscous continuum. The observations are more consistent with the original "cage" picture of Rabinowitch[10] in which the separating atoms are held together by specific solvent molecules. As the molecular weight of hydrocarbons increases, a situation is reached where the iodine atoms are effectively pushing against only a few segments of molecules rather than against the molecules as a whole. Escape of iodine atoms will then take place only if the direction of recoil is such as to permit an atom to force its way between two adjacent molecules and the probability of escape will be almost independent of the sizes and complexities of the parts of each solvent molecule that were not directly affected. Beyond a certain limit, increases in molecular complexity will increase viscosity but will be virtually without influence on quantum yield. Such an interpretation would require preservation of the distinction between "primary" and "secondary" recombination,[11] while models regarding the solvent as a continuum do not need to make this distinction.

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[10] E. Rabinowitch and W. C. Wood, *Trans. Faraday Soc.*, **32**, 1381 (1936).

[11] R. M. Noyes, THIS JOURNAL, **77**, 2042 (1955).

EUGENE, OREGON

[CONTRIBUTION FROM THE CHANDLER LABORATORY OF COLUMBIA UNIVERSITY AND FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF OREGON]

The Dependence on Wave Length of Quantum Yields for Iodine Dissociation

BY LENORE F. MEADOWS[1] AND RICHARD M. NOYES[2]

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Quantum yields for iodine dissociation have been measured at 25° in hexane and in hexachlorobutadiene-1,3 for six wave lengths from 4047 to 7350 Å. For these wave lengths, the initial kinetic energies divided between the separating atoms ranged from 35.0 to 3.3 kcal./mole. Quantum yields at 4358 A. are in fair agreement with values predicted by a theory that treats the surrounding solvent as a viscous continuum and that uses no parameters not capable of independent measurement; the quantum yields at 7350 Å. are in good agreement with the predictions of the same theory for eventual separation of two atoms starting apart with only thermal kinetic energies. However, the quantum yields at intermediate wave lengths fail to reproduce the pattern predicted by the theory. The discrepancies directly support a proposal originally made by Rabinowitch that solvent molecules push together two atoms separated by less than a certain critical distance but that the solvent molecules preferentially push apart atoms separated by a little more than this critical distance. The data also suggest that for atoms separating with kinetic energies of only a few kcal./mole the probability of escape is much more dependent on the chance distribution of solvent molecules in space than it is on the absolute value of this small kinetic energy of separation. Any further quantitative theoretical advance must specifically recognize the discrete molecular nature of the solvent.

Introduction

This study is part of a program to learn more about molecular interactions in liquids by measuring quantum yields for iodine dissociation under a variety of conditions. When the molecule absorbs a quantum containing more than enough energy to break the bond, the excess appears as kinetic

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[1] Based on the Ph.D. Dissertation of Lenore F. Meadows. The original dissertation and microfilms thereof are available from the Library of Columbia University, New York, N. Y.

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