

THE CORRELATION OF PHOTOCHEMICAL REACTIONS IN GASES WITH THOSE IN SOLUTION¹

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Developments in the interpretation of atomic and molecular spectra have been useful to photochemistry primarily in connection with gaseous reactions. For it is ordinarily only in the gaseous state that substances give sufficiently detailed spectra to permit of precise interpretation; an absorption spectrum which is discrete in the gaseous state usually becomes continuous in a condensed state or in solution. Furthermore, the formulas of kinetic theory which are needed in the discussion of reaction kinetics have had a sounder basis in their application to gases than to liquids. It is natural, then, that in treating solution reactions, free use has been made of information concerning gaseous substances. In view of this, it appeared to be of interest to review such existing data as permit comparison of photochemical processes in gases with those in liquids. A major part of the present survey consists in the comparison of data in cases where the same reaction has been studied in gas and in solution, especially in inert solvents.

Photochemical reactions are conveniently considered to involve two types of process: (1) those primary processes accompanying the absorption of radiation, and (2) those subsequent secondary processes which proceed without the further intervention of radiation. Consequently it will be convenient here to consider the effect of solvent on these processes separately.

In general, substances exhibit in solution absorption spectra which differ from those given in the gaseous state even aside from the broadening of absorption lines in solution; for example, the maximum visible absorption of iodine in alcoholic solution is in the blue, while that for gaseous iodine is near the green. However, with inert non-polar solvents or with inert solvents which are similar to the solute, the alteration is often relatively slight. When mercury is dissolved in hexane, although the first resonance line is considerably broadened (5) and separated somewhat into two components, nevertheless the absorption still occurs in the immediate

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neighborhood of the frequency of the gaseous line 2537; furthermore, the integral absorption coefficient in the solution is little different from that in the gas (33). The unchanged position of the absorption shows that the difference between the energies of an excited and a normal mercury atom is the same in solution as in gas; equality of the integral absorption coefficient signifies equal probability of electronic transition. Further examples of both qualitative and quantitative similarity in absorption spectra in the gaseous state and in solution are afforded by the halogens in carbon tetrachloride, chloroform, and carbon bisulfide, by hydrogen peroxide (41) in water, and by hydrogen sulfide (26) in water and in hexane.

When such similarity between the gaseous and solution absorption spectra exists, it is reasonable to assume that absorption is accompanied by the same electronic transition in both cases. In spite of this, the outcome of the absorption process may be considerably modified in solution. If the gaseous absorption is discrete and results in an excited molecule, then in solution the excited molecule may either (1) have its excitation energy degraded to thermal motion by collision with solvent molecules, or (2) dissociate on collision with solvent molecules if its energy be sufficient. (If the solvent be not inert, there exist further possibilities of reaction with it.) If the gaseous absorption is continuous and results in dissociation, then in solution collision with a solvent molecule before dissociation is completed may remove energy to prevent its occurrence. Even if dissociation does occur, there is in solution an increased probability of immediate recombination of the same dissociating partners resulting from the short mean free path, which leaves them initially in close proximity. This last process has been discussed by Franck and Rabinowitsch (19), and has been called by them "primary recombination" to distinguish it from the "normal" uniting of particles which were not previously partners. Similar possibilities exist if the gaseous absorption is in a predissociation region; here, however, opportunity for deactivation is increased by the longer interval before dissociation, especially with polyatomic molecules (20).

In order to obtain some idea of what to expect of the effect of solvent on processes subsequent to those mentioned, we may look to the results obtained with purely dark reactions. In general the rates and temperature coefficients of ordinary reactions in solution are considerably dependent upon the solvent used, and this dependence is highly specific and in large measure unpredictable. Nevertheless, Moelwyn-Hughes, who has extensively reviewed this field (28), has concluded that with inert non-polar solvents, such as carbon tetrachloride, rates and temperature coefficients not very different in gas and in solution may be expected, and that the application of gas kinetic theory collision rates to solutes may be made with some confidence.

One type of reaction step, namely the bimolecular association of atoms, may be expected to proceed much more rapidly in solution, for the co-operation of a third colliding body is necessary in order to give rates of importance. When the molecule resulting from a bimolecular association contains a sufficient number of atoms, then, as Kassel has shown (25), the necessity for a third body to stabilize the collision is no longer present. In this case, grounds for predicting a more rapid association in solution are absent.

After this outline of some effects which may be expected, individual cases, for which data are given in table 1, will now be considered. It may be well to summarize at the outset and say that for those cases for which data are available, where the same reaction proceeds in the gas and in solution or liquid, it proceeds with about the same quantum yield or same specific rate in each or else proceeds more rapidly in the gas.² It is usually difficult to be certain just which dissipational effect preponderates in any individual case.

Nitrogen dioxide shows a predissociation spectrum, the products of the predissociation being presumably NO and O (both normal). It shows a photochemical threshold (10, 30) approximately at the predissociation limit, with no decomposition in the band region and quantum yields of about two NO₂ decomposed per quantum (products: 2NO and O₂) in the ultra-violet. In gaseous mixtures with nitrogen pentoxide, the net result of illumination is sensitized decomposition of the nitrogen pentoxide; and this may be regarded simply as the usual decomposition of nitrogen dioxide followed by rapid reaction of nitric oxide with nitrogen pentoxide (3, 22). In carbon tetrachloride solution the decomposition is relatively small (22).

It is interesting to compare the behavior of chlorine dioxide with that of nitrogen dioxide. Gaseous chlorine dioxide shows bands with fine structure extending from the green into the ultra-violet; the bands become diffuse at 3750 A.U., and this is attributed to predissociation. In carbon

² Note added September 4, 1935: Dr. R. A. Ogg, Jr., has kindly called the writer's attention to one case where existing data are not in agreement with this generalization. At wave lengths corresponding to the continuous absorption of ethyl iodide, gaseous ethyl iodide undergoes very little decomposition, whereas a considerably greater production of free iodine has been found with liquid ethyl iodide and with ethyl iodide in hexane and in benzene solution. This case is discussed at length by West and Ginsburg (WEST, W., AND GINSBURG, E.: J. Am. Chem. Soc. **56**, 2626 (1934)).

It has been contended (STOBBE, H., AND SCHMITT, P.: Z. wiss. Phot. **20**, 57 (1920)) that this iodine production is due to oxidation. Although recent investigators have not ignored the possible effect of oxygen here, one might, in view of the exceptional nature of this case, wish for experiments in which rigorous exclusion of oxygen and water was assured.

TABLE 1

Quantum yields of reactions in gaseous and condensed systems

REACTION	WAVE LENGTH	QUANTUM YIELDS		
		Gas	CCl ₄	
$N_2O_5 \rightarrow NO_2 + \frac{1}{2}O_2$ (sensitized by NO_2)	4358	0		
	4050	0.7	0.03	
	3660	1.8	0.02(0.15)	
	3130	1.9		
$2ClO_2 \rightarrow Cl_2 + 2O_2$	3000	(Much ClO_3 formed; chains)	CCl ₄	Water
	3130		2.1	1.0
	3665		2.2	0.76
	4050		2.2	0.50
	4358		1.0	0.20
$2Fe(CO)_5 \rightarrow Fe_2(CO)_9 + CO$	2540	Gas	Liquid	
	3000		1.89	
	3660		1.86	
	4050		1.76	
	4358		1.66	
$2HI \rightarrow H_2 + I_2$	2070	Gas	Liquid	Hexane (0.8 molal)
	2220	1.98		1.52
	2530	2.08		
	2820	2.06		1.78
	3000		1.84	
$H_2S \rightarrow H_2 + S$	2070	Gas	Hexane	Water (0.115 molal)
	2200	2.1	0.97	0.43
	2530		0.95	0.32
$N_2O_5 \rightarrow 2NO + \frac{1}{2}O_2$	2800	Gas	CCl ₄	
	2650	0.6	0.04	
$2Cl_2O \rightarrow 2Cl_2 + O_2$ (also ClO_2)	2537	Gas	CCl ₄	
	3130	4.5		
	3650	3.5		
	4358	3.4		
		3.2	1.8	

TABLE 1—*Concluded*

REACTION	WAVE LENGTH	QUANTUM YIELDS			
		Gas	Liquid	Water	Hexane
$2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2$	~2100	0.14 to 0.25	No decomposition	No decomposition	Little NH_3 decomposition. Sensitized decomposition of hexane
$\text{C}_2\text{Cl}_4 + \text{Cl}_2 \rightarrow \text{C}_2\text{Cl}_6$	4358	Chains dependent on (Cl_2) and (I_{abs}) but about same in gas and CCl_4			
C_2Cl_4 oxidation (sensitized by Cl_2)	4358	Gas		CCl_4	
		~375 at 0.01 atm.		~1 at 0.04 m.	
CHCl_3 oxidation (sensitized by Cl_2)	4358	Gas		CCl_4	
		~100 at ~0.1 atm.		~0.6 at 0.05 m.	

tetrachloride solution decomposition simply into Cl_2 and O_2 occurs with quantum yields (7, 29) of 2 at 4150 A.U. and less and 1 at 4358 A.U. At least at the shorter wave lengths, primary deactivation by solvent apparently does not occur, unless the yield of 2 be regarded as fortuitous. In the gaseous state, chain reaction with the formation of ClO_3 occurs (37). In aqueous solution the solvent is not inert, and HCl and HClO_3 are formed (7).

Another substance showing a predissociation spectrum is ammonia; the absorption process is interpreted as resulting in NH_2 and H . However, at room temperature only about 0.25 NH_3 or less is decomposed per quantum (31). Various experiments have led to the belief that the lowness of the yield is due, at least in part, to re-formation of NH_3 from H and NH_2 or N_2H_4 ; the most recent of these experiments involves the photolysis of ordinary ammonia in the presence of atomic deuterium with the formation of deuterio-ammonias (39). In the pure liquid state, ammonia suffers no appreciable decomposition (31), nor does it do so in aqueous solution (17). In hexane solution little decomposition of ammonia results, but instead an ammonia-sensitized decomposition of the hexane (17). It has been assumed that in this case the ammonia is deactivated before dissociating, its energy serving to decompose the hexane.

Iron pentacarbonyl, $\text{Fe}(\text{CO})_5$, is decomposed in the gaseous state into carbon monoxide and diferro-nona-carbonyl, $\text{Fe}_2(\text{CO})_9$, with a quantum

yield (16) of about $2\text{Fe}(\text{CO})_5$. In the pure liquid state yields (46) only a few per cent smaller have been found.

A well-known reaction in which the gaseous absorption is clearly continuous is the decomposition of hydrogen iodide. In the gas two molecules of hydrogen iodide are decomposed per quantum absorbed (43). There is little doubt that the gaseous decomposition proceeds through the reactions:



Pure liquid hydrogen iodide decomposes with substantially the same quantum yield (4) and may be supposed to do so by the same mechanism. If, however, owing to the frequency of collision with other hydrogen iodide molecules in the liquid, the reaction forming H_2 be supposed to occur before the completion of dissociation, a formally different mechanism may be written (19):



In hexane solution lower values, 1.2 to 1.8, dependent on the wave length and somewhat on the concentration, have been obtained (44). These lower values are possibly due to either deactivation or primary recombination, although it is not clear why either of these processes should lead to a concentration effect in dilute solution. Normal recombination of hydrogen atoms could lead to a concentration effect, and could also lead to lower quantum yields at the shorter wave lengths, where the absorption coefficient of hydrogen iodide is larger and the local concentration of hydrogen atoms produced with a given intensity is higher.

Gaseous hydrogen sulfide similarly has a continuous absorption. Whether the absorption process is accompanied by dissociation into H_2 and S or into H and HS is not certain ($2\text{H} + \text{S}$ is not energetically possible). At pressures of 250 mm. or less, two molecules of hydrogen sulfide are decomposed per quantum (38), and with either primary products this yield could result from a mechanism analogous to that for hydrogen iodide decomposition. At higher pressures, yields of 3 to 4 have been found but not very satisfactorily accounted for. In hexane solution yields of close to 1 have been found, with no evident concentration or wave length dependence (45). Unless this value of unity be regarded as accidental, it is most readily accounted for as resulting from complete normal recombination of H atoms (or of S atoms) with solvent molecules as third bodies. In aqueous solution the quantum yields are still smaller, and decrease with increasing wave length.

Only continuous absorption starting at 3050 A.U. has been found (42) with gaseous nitrogen pentoxide. This long wave limit corresponds closely to the energy change in the reaction $\text{N}_2\text{O}_5 \rightarrow 2\text{NO}_2 + \text{O}$. The quantum yield (22) of gaseous decomposition is, however, only 0.6. This is difficult to account for with the above primary process; for if reoxidation of NO_2 by O occurs here, it is not evident why it should not do so in the decomposition of NO_2 . A rather large depression of the yield occurs in carbon tetrachloride solution (22).

Another substance whose gaseous absorption is continuous is chlorine monoxide. The gaseous photochemical decomposition gives Cl_2 , O_2 , and small amounts of ClO_2 and other oxides. The more recent values of the quantum yields (18, 35) are 3.2 to 3.5 Cl_2O decomposed at the longer wave lengths and 4.5 Cl_2O at 2537 A.U. At the longer wave lengths the quantum yields remain unchanged when chlorine instead of chlorine monoxide is the primary absorber. In view of this fact, secondary decomposition by chlorine atoms evidently occurs. The numerical values of the quantum yields suggest also short-chain decomposition. In carbon tetrachloride solution the yields are somewhat smaller (12), and these smaller values have been attributed (18) to the effect of solvent in stabilizing chain-breaking steps.

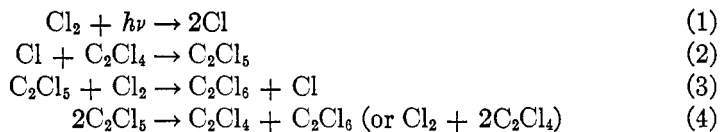
In view of the photochemical importance of the halogens, it is of especial interest to know the products of the absorption process under various circumstances. When the absorption corresponds to the continuum, there is little doubt that atoms result, although these may be subject to a certain amount of primary recombination in solution. However, the fact that the chlorine-sensitized decomposition of ozone occurs in carbon tetrachloride solution with yields (8) of close to 2 suggests that primary recombination is not large in this particular case.

The chlorination of tetrachloroethylene has been studied both in gas (11) and solution (27) with the wave length 4358 A.U., which lies in the gaseous continuum. In the gaseous state the local rate of reaction is given by

$$-\frac{d(\text{Cl}_2)}{dt} = k(I_{\text{abs}})^{\frac{1}{2}}(\text{Cl}_2)$$

Quantum yields (dependent on (Cl_2) and (I_{abs})) of several hundred have been measured. The value of k has been found to be $147 \text{ einsteins}^{-\frac{1}{2}} \times \text{cm.}^{\frac{1}{2}} \times \text{sec.}^{-\frac{1}{2}}$ at 26°C . In carbon tetrachloride solution a rate expression of the same form is found when sufficient tetrachloroethylene is present, and the value of k is 165 at 22°C . The value of k for the gas is subject to some uncertainty, but can hardly be greatly different from that

for the solution. A simple chain mechanism which is in agreement with these facts is:



With long chains, this leads to the empirical rate expression with $k = k_3/k_4$. The rate-determining reactions are accordingly reactions 3 and 4, and since these are not bimolecular associations, there is no ground for predicting a solvent effect on either.

When oxygen is present in addition to chlorine and tetrachloroethylene, oxidation instead of chlorination occurs, the products being trichloroacetyl chloride and some phosgene. In this case the rate is proportional to the first power of the light intensity, and in the gas long chains again occur (11). In solution the chains are several hundredfold shorter (13). Since the elementary absorption process is presumably the same as in the absence of oxygen, the different effect of solvent in the chlorination and in the oxidation clearly lies in the subsequent processes; for the oxidation, these are not well understood. In the chlorine-sensitized oxidation of chloroform, long chains in the gas but not in carbon tetrachloride solution are also found (9).

When an excited halogen molecule is produced by a wave length of the band region, it may still possess sufficient energy for dissociation into normal atoms, and either this or deactivation may occur when the excited molecule enters into collision. In the case of bromine, indirect evidence that dissociation, instead of degradation to thermal energy, occurs both in the gaseous state and in solution is furnished by a number of photochemical reactions. In the gaseous state several reactions have been found to proceed with substantially the same yield with wave lengths on either side of the convergence; among these are the formation of hydrogen bromide (23), the bromination of cyclohexane (24), the bromination of acetylene (6), and the bromine-sensitized decomposition of chlorine dioxide (36, 37). In the liquid state, yields only slightly smaller on the long-wave side than on the short have been reported in the bromination of cinnamic acid in carbon tetrachloride solution (2) and in the bromination of liquid benzene (32); in the bromination of maleic ester and its rearrangement to fumaric ester, yields about half as large at 5461 A.U. as at 4358 A.U. have been found (15).

For gaseous iodine there is direct evidence that at least some iodine atoms result when the gas is illuminated by wave lengths longer than 5100 A.U. in the presence of argon, for under these circumstances absorp-

tion lines due to atomic iodine appear in the ultra-violet (40). For iodine in solution, the data are not concordant. In the iodine-sensitized rearrangement of *allo*-cinnamylidene acetic acid into the normal form, 5461 A.U. has been reported (21) as more effective than 4358 A.U. both in benzene and in carbon tetrachloride solution; this appears inexplicable and invites reëxamination. In the iodine-sensitized decomposition of ethylene iodide in carbon tetrachloride solution, quantum yields only one-fifth as great for 5461 A.U. as for 4358 A.U. have been measured (34); the conclusion drawn from this result was that the excited iodine molecule usually lost its energy on collision with solvent molecules. However, in view of the fact that this reaction proceeds at a rate proportional to the square root of the intensity of illumination, ordinary measurement of quantum yield alone does not permit such a conclusion, for when the rate of a reaction is not proportional to the intensity, the over-all quantum yield depends on the distribution (1) of radiation through the reacting medium, and this distribution changes in general with the absorption coefficient. With due allowance for this fact, the effect of wave length on the sensitized ethylene iodide decomposition has recently been remeasured (14). With local rates of reaction represented by

$$\frac{d(I_2)}{dt} = k(I_{\text{abs}})^{\frac{1}{2}}(C_2H_4I_2)$$

values of k in carbon tetrachloride solution at 76.6°C. were found to be 0.425 einstein⁻¹ × cm.³ × sec.⁻¹ at 4358 A.U., 0.396 at 5461 A.U., and 0.368 at 5780 A.U. If β be the fraction of the absorbed quanta which result in dissociation of iodine molecules, directly or on subsequent collision, then for two different wave lengths

$$\beta_1/\beta_2 = k_1^2/k_2^2$$

and

$$\beta_{4358}:\beta_{5461}:\beta_{5780} = 1:0.87:0.75$$

It appears then that with iodine, wave lengths corresponding to the band region are little less effective than those of the continuum in producing dissociation in carbon tetrachloride solution.

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DISCUSSION

PROFESSOR FRANCK: I am very much impressed by the fact that Dr. Dickinson could study so many interesting photochemical reactions under conditions which allow a comparison between gaseous and liquid states. In regard to the conclusion that in carbon tetrachloride solution a considerable percentage of absorptions by halogens leads to dissociation, I wish to mention that this seems to be in disagreement with general conclusions which Rabinowitch and I have presented previously (19). I would expect a very small yield, because a very large back reaction should take place.

The difference between the absorption region which belongs in the gaseous state to a discrete absorption spectrum and the region which is a continuum in the gaseous state is not so important for reactions in the liquid phase. In the gaseous state the absorption in the discontinuum forms an excited molecule with an average life-time of $\sim 10^{-8}$ seconds or longer. The absorption in the continuum also gives an excited molecule, but with a life-time equal to the time of one oscillation $\sim 10^{-13}$ seconds. The probability of impacts in the latter case for normal pressure is negligible. But in a liquid the particles are permanently in a state of collision, so that the difference caused by the different life-times vanishes. What remains is only the difference in frequencies; that will mean the smaller or greater surplus of the energy absorbed against the heat of dissociation. In cases in which the yield is of the order of magnitude of 1, we should always expect a reaction (for instance, with the molecules of the solvent) which forms at least one saturated molecule.

DR. OGG: The very low yield for primary photodissociation in solutions which Professor Franck postulates seems difficult to reconcile with data on the iodine-sensitized photodecomposition of ethylene iodide in carbon tetrachloride solution. Here a reaction of the iodine atoms (produced by photodissociation) with the solvent is out of the question. The velocity of the reaction $I + C_2H_4I_2 \rightarrow C_2H_4I + I_2$ in carbon tetrachloride solution was measured in the case of iodine atoms produced by the known *thermal* dissociation of iodine molecules. Comparison with the photochemical reaction allows of calculation of the steady state concentration of iodine atoms in the illuminated solutions. From the values for the steady state concentration, it follows that a quantum efficiency for the primary photodissociation of iodine molecules as small as that assumed by Professor Franck would necessitate a rate of recombination of iodine atoms which is improbably small in comparison with known rates of the trimolecular gas phase recombination of halogen atoms.

PROFESSOR FRANCK (communicated): I should like to ask Dr. Ogg if he is content with the statement, "Franck and Ogg agreed in a private

discussion that the case mentioned by Dr. Ogg is a special case which is not contrary to the discussion remarks made by Franck.”

DR. OGG (communicated): I regret to state that I cannot agree completely with Professor Franck's statement. In my opinion the ethylene iodide decomposition, far from being a special case, is a very good example for comparison of rates in solution and in gas phase. I do agree, however, that the interpretation of experimental results so far obtained for this reaction is not necessarily in disagreement with the low efficiency postulated by Professor Franck for primary photodissociation in liquid systems. The essential vagueness of the kinetic picture of trimolecular recombination of free atoms in liquids makes a sharp decision regarding this point very difficult. A satisfactory picture of collision processes in solution must be obtained before the point under discussion can be wholly clarified.