SOME REMARKS ABOUT FREE RADICALS AND THE PHOTOCHEMISTRY OF SOLUTIONS.

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I. Free Atoms and Radicals in Photochemistry of Gases and Liquids.

The majority of photochemical processes in gases take place through the intermediary of free atoms or radicals. A great number of photochemically sensitive molecules exhibit spectra of completely continuous character ; another large group show but feeble discontinuous bands as compared with strong regions of continuous absorption. Only a few molecules, mostly of the simplest di- or triatomic structure (NO, CO, I_2, NO_2, SO_2, etc.), possess a strong discontinuous absorption ; C_6H_6 is one of the rare examples of more complicated molecules of this kind.

The primary effect of absorption, in the case of a continuous spectrum in a gas, is always dissociation, and the products of dissociation will in most cases be free atoms or radicals. (An exception is provided for example, by organic acids, which give a primary dissociation into CO_2 and hydrocarbons.: $R . COOH + h\nu \rightarrow R . H + CO_2$.)[1] The lapse of time between the absorption of light and the dissociation of the molecule varies from the order of 10^{-13} sec. (in truly continuous spectra, corresponding to a repulsive potential-curve in the excited state of the molecule) to 10^{-10} sec. (in some predissociation-spectra).[2] The probability of a molecular collision occurring before the dissociation has been accomplished is very small (of the order of 10^{-4} for truly continuous spectra at atmospheric pressure) and may be disregarded.[3] Thus we can assume, that the formation of primary dissociation products in gases proceeds with a quantum yield of $\gamma = 1$.

In several examples—*e.g.*, the reaction $Br_2 + H_2 = 2HBr$ where

[1] L. Farkas and O. H. Wansborough-Jones, *Z. physik. Chem.*, **18B**, 124 (1932).
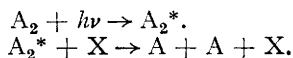[2] E.g. in the case of N_2O, M. Volmer and H. Kummerow, *Z. physik. Chem.*, **9B**, 171 (1930).
[3] Still, in some special cases this possibility can play a certain rôle, as we have pointed out in a previous note about the chlorine-hydrogen reaction (*Z. Elektrochemie*, **36**, 794, 1930).
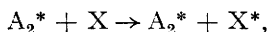
the same photochemical reaction has been studied in the spectral con-
tinuum and in the band-region—a close analogy in the kinetics of both
cases has been found ; these results lead to the notion that the linear
absorption also ends in a dissociation, though in a secondary way by col-
lisions between the excited molecules and other molecules present in
the gas.[4] Schemes also have been proposed for a great number of chain-
reactions and explosive reactions in gases, based on the assumption that
free radicals or atoms are reformed in each step of the process.

In nearly all photochemical discussions this " atomic " mechanism
of reaction-chains has been obviously preferred to the " energetic,"
in which the chains are propagated by excited (for instance, strongly
vibrating) molecules.

It may be that this preference was not always entirely based on phy-
sical considerations, but also on the greater simplicity of discussion.   The
atomic mechanism can always be represented through a set of ordinary
chemical equations.   It offers many fewer different possibilities than
the " energetic " mechanism.   It is much simpler to accept a dissociation.

$$A_2 + h\nu \rightarrow A_2^*.$$
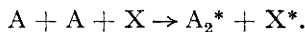$$A_2^* + X \rightarrow A + A + X.$$

as the only result of collisions between activated molecules A_2 and any
normal molecule present in the gas, than to discuss all possibilities of
distribution of energy between the collision-partners,

$$A_2^* + X \rightarrow A_2^* + X^*,$$

or all possibilities of chemical reactions of A_2^* with X.

It is not improbable that the excited molecules play a greater rôle
in the propagation of reaction-chains in gases then has been generally
ascribed to them.   When two atoms or radicals recombine in a triple
collision, it is not legitimate to postulate that in every case this event
means a breaking-up of the chain.   The correct formula of a recombina-
tion-process is

$$A + A + X \rightarrow A_2^* + X^*.$$

rather then $A + A + X \rightarrow A_2 + X$, as ordinarily written.   The energy
transported away by the molecules A_2^* and X^* may often be great enough
to act as activation-energy in a subsequent collision with a suitable
partner.   But, even if we admit that the rôle of activated (especially,
of strongly vibrating) molecules in the propagation of reaction-chains
has often been under-estimated, we must agree that in gaseous photo-
chemical reactions the formation of free atoms and radicals plays a pre-
dominant rôle (a) as the " normal " first step immediately following the
absorption of light, and (b) as the most important way for the propaga-
tion of reaction-chains.

The purpose of this note is to discuss the rôle of free atoms and
radicals in photochemical reactions in liquid systems.   The general
conclusion is that in liquids the probability of reactions proceeding
through activated molecules must be increased and the rate of formation
of free atoms and radicals must be generally lower, than in gases.   This
statement holds for the *first step* of photochemical reactions ; on the other

[4] W. Jost, *Z. physik. Chem.*, **134,** 92, 1928 ; **3B,** 95, 1929.   On the other hand
the experiments of R. G. W. Norrish, *J. Chem. Soc.* (1929), 1158, 1605, 161
indicate that in the case of NO_2 no reaction occurs at all so long as there is no
direct dissociation $NO_2 + h\nu \rightarrow NO + O$;   excited NO_2^*-molecules seems to
be completely ineffective.

hand the propagation of reaction-chains in liquids can take place practically *only* with the help of free unsaturated particles, because excited molecules will be quickly deactivated through collisions with the molecules of the solvent.[5] The lower rate of formation of free atoms or radicals together with the impossibility of reaction-chains being propagated by activated molecules must lead to a general lowering of the quantum-yield of chain-reactions in liquids. This lowering must be attributed not only to a smaller mean *length* of the chains ; the *number* of chains that are really started under given conditions of light-intensity and concentration will also be affected.

There are two possibilities of photochemical reactions not involving free atoms or radicals : (1) photochemical dissociation in two saturated molecules ; *e.g.*, $HCOOH + h\nu \rightarrow H_2O + CO_2$, or at least in one molecule and one radical ; *e.g.*, $Cl_2O + h\nu \rightarrow Cl_2 + O$; (2) chemical reaction through the intermediary of excited molecules, *e.g.*, $Br_2 + h\nu \rightarrow Br_2^*$; $Br_2^* + RCH = CHR \rightarrow (RCHBr)_2$; or $HBr + h\nu \rightarrow HBr^*$; $HBr^* + HBr \rightarrow H_2 + Br_2$ (in pure liquid hydrobromic acid). In liquids and solutions the activated state Br_2^* or HBr^* need not be one of long life ; a life time of 10^{-13} sec. which must be attributed to every unstable dissociating molecule is long enough to permit collisions with neighbouring molecules of the liquid.

When a photochemical reaction in solution or in a pure liquid shows a primary quantum yield exactly or nearly equal to unity without a pronounced influence of temperature, light-intensity or wave-length, we must consider this as an evidence for a mechanism involving no atoms or radicals. On the other hand reactions proceeding through the intermediary of free radicals or atoms must exhibit characteristic deviations from the equivalency-law, depending on wave-length, concentration, light-intensity and temperature.

II. Dissipation and Primary Recombination-Effect.

In a *gaseous* system every act of absorption in the continuous region of the spectrum leads to a dissociation. The absorption-spectra of *liquids* or *solutions* are nearly always continuous ; but this property cannot be considered as a proof for dissociation as the primary effect of absorption. The continuous character may be due to : (*a*) the influence of the electric fields of the surrounding molecules (asymmetrical Stark-effect), and (*b*) the broadening of lines resulting from the shortening of the lifetime of the excited molecules as a consequence of collisions with molecules of the solvent. Those collisions can lead (*a*) to a return to the ground-state with dissipation of the absorbed energy, (*b*) to a chemical reaction with a molecule of the solvent or with another molecule present in the surrounding sheet of the liquid, or (*c*) to a dissociation of the activated molecule as discussed on page 127. Dissociation provides thus only one of many possibilities of line-broadening through collisions.
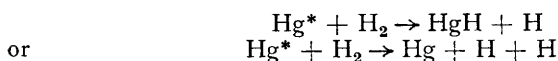
Let us consider for example the spectrum of bromine. In the vapour-state it is continuous below $\lambda = 5100$ Å. ; in this region every absorbed quantum means a dissociated molecule. Between 5000 and 6000 Å. the spectrum is discontinuous, but the absorbed quantum is greater

[5] Exceptions may occur, as is shown by the existence of fluorescence in liquids ; but activated molecules which can conserve their activation-energy through many thousands of collisions with molecules of the solvent will probably be ineffective also in transmitting this energy to other collision-partners.

than the dissociation-energy ; thus a dissociation through collision of an activated molecule with a normal molecule is possible, and the number of Br atoms formed will depend on pressure and character of the gas-mixture. With $\lambda > 6000$ Å. the probability of dissociation will decrease and quickly reach zero.

In a solution of Br_2 in CCl_4 or $CHCl_3$ the general shape of the absorption-curve is not altered, but the whole spectrum is continuous. In the region between 5000 and 6000 Å. the probability of formation of free Br atoms may be greater in solution than in the gas (especially in a gas of low pressure), since in solution every excited molecule must suffer collisions. This is obviously an example of the only possible case in which the substitution of a solution for a gas may lead to an increased production of free atoms or radicals. This effect, occurring only in a relatively narrow spectral region, would generally be over-shadowed by a strong effect in the opposite direction, tending to decrease the rate of formation of free atoms in the whole region of continuous absorption. This effect is the *dissipation* of the absorbed energy through collisions of the second kind, and the *primary recombination* of the dissociation-products : *i.e.*, a recombination occurring before these products have reached a statistical distribution in the liquid.

A. Dissipation - Effect. — The experiments on the quenching of fluorescence in gases show that in every collision of an electronically excited atom or molecule with a second particle there is a definite probability of dissipation of the activation-energy. In special cases of electronic resonance the whole energy is transferred to the collision-partner and retains its character as electronic activation. Generally the energy will be distributed between all degrees of freedom of both colliding bodies. The probability of dissipation occurring already in the first collision is very low, if the collision-partner is a monatomic molecule, possessing only *translational* degrees of freedom. The probability of transformation of the electronic activation-energy into *vibrational* energy of the partner is only high if there is good resonance between the amount of activation-energy present and one or a few vibrational quanta of the colliding molecule (the transfer of excited Hg atoms from the $^3P_1$-state to the metastable $^3P_0$-state in collisions with molecules of N_2 and H_2O provides an example of this kind). The highest probability of deactivation occurs when the colliding molecule undergoes a chemical change, as for example in the quenching of mercury resonance-fluorescence by hydrogen ; in this case one of the processes

$$Hg^* + H_2 \to HgH + H$$
or
$$Hg^* + H_2 \to Hg + H + H$$

occur in every kinetic collision.

Both kinds of interaction with the solvent (conversion of the activation-energy into vibrational energy and chemical changes of colliding molecules) must occur with a definite probability when a molecule in the middle of a liquid is excited through absorption of light.

One may suppose that at least the probability of conversion into vibrational energy, which means a total loss of the activation-energy from the photochemical point of view, must be low since the absorbed quanta are relatively great (visible or ultraviolet light) and does not correspond to the vibrational quanta of the solvent. But there exists a difference between a " stable " activated state, say of the Hg atom, and a dissociating unstable state, say of Br_2^*. This is illustrated by

Fig. 1 which represents two potential-curves of a molecule: a stable ground-state ABCD and an unstable activated state A'B'C'D'. The molecule may be excited to a state represented by the point C'; it will then dissociate along the curve C'B'A', and will, if left to itself, derive at A' after a time-lapse of about 10^{-13} sec. We assume, that at A' (nuclear distance $z - z_0$) the coupling between the dissociation products has practically vanished. On the whole path between C' and A' there still exists a possibility of a return to the stable ground-state ABCD by a collision of second kind. The probability of this process may be small at C', where the whole energy-quantum CC' must be taken away; but it will rise with increasing nuclear distance; at B' only the small amount of energy BB' must be converted into vibrational energy of the colliding molecule, and the entire remainder CC" — BB' can reside as vibrational energy in the absorbing molecule itself. In this way the pure dissipation of the absorbed energy, with conversion into vibrational energy (partly of the absorbing molecule itself, partly of the surrounding molecules of the liquid), cannot be considered as improbable, and this effect alone must already lead to an appreciable loss of energy and to a marked decrease of the quantum-yield of every primary dissociation in liquid systems below the value $\gamma = 1$.
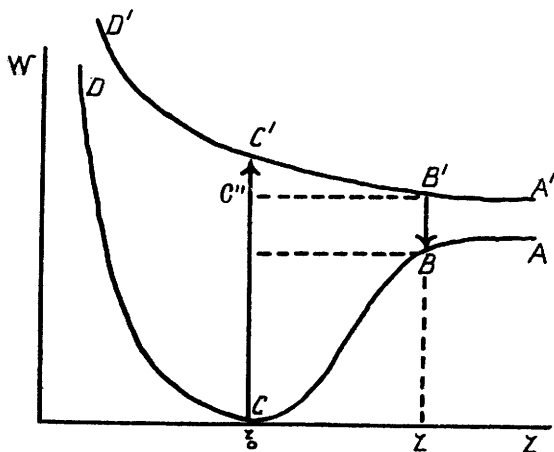

FIG. 1.

The second possibility of preventing the dissociation (i.e. a chemical interaction between the activated molecule and the solvent) will moreover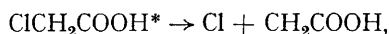 nearly always not be negligible. The most inert of our usual solvents (carbon tetrachloride, saturated hydrocarbons, etc.), contain bonds with dissociation-energies of not more than 3 or 4 electron volts. There is no reason why activated molecules that have absorbed quanta of 3 to 5 electron-volts should be wholly incapable of reacting in some way with the molecules of the solvent. For example, why should an excited Br_2^*-molecule possessing 4 volts activation-energy not react with a CCl_4-molecule, in giving CCl_3Br and ClBr, or CCl_3, ClBr and Br or simply in dissociating CCl_4 in CCl_3 and Cl? Reactions of this kind may later revert in the dark, in which case the ultimate result will be, as above, a simple dissipation of the light-energy. In other cases, the chemical changes may be irreversible; then the ultimate effect will be a new kind of photochemical reaction, not occurring in the gaseous phase.

Let us consider as an example the bromination of benzene (or of another aromatic molecule). In a previous note [6] one of us has dis-

[6] E. Rabinowitsch, *Z. physik. Chem.*, **19B**, 190, 1932.

cussed the mechanism of this reaction in the pure liquid state and in solution in CCl_4 and proposed a scheme, in which the primary dissociation in Br-atoms leads to a *substitution*, *i.e.*, to the formation of C_6H_5Br (in a short chain), while the reaction between activated Br_2^*-molecules and C_6H_6 results chiefly in an *addition*, *i.e.*, in a formation of $C_6H_6Br_6$. It would be interesting to study this reaction in the gaseous phase ; in our opinion we must (using the continuous region of absorption of Br_2) obtain C_6H_5Br as the chief bromination-product in the gaseous phase.

We have already suggested on page 121 that reactions of activated molecules, involving no dissociation at all, may be responsible for many photochemical reactions in liquids which have been found to proceed with the " full " quantum efficiency of $\gamma = 1$. For example, in the photo-hydrolysis of $ClCH_2COOH$ (a reaction for which Rudberg[7] found a quantum-yield $\gamma = 1$), we may accept as the first step instead of the dissociation :

$$ClCH_2COOH^* \rightarrow Cl + CH_2COOH,$$

some reaction between activated unstable $ClCH_2COOH$-molecules and water-molecules ; for instance, simply

$$ClCH_2COOH^* + H_2O \rightarrow OHCH_2COOH + HCl.$$

B. Primary Recombination-Effect.—Even though a molecule in solution may happen to dissociate after absorption, and the radicals or atoms formed in this way separate with a certain amount of kinetic energy, this excess energy will be at once lost in collisions with the solvent and the particles will be stopped at a distance of one or few molecular diameters from one another. The appropriate picture

FIG. 2.

of a strongly-illuminated solution—say of bromine in CCl_4—is thus not one showing free bromine atoms distributed at random in the liquid (as Br_2-molecules really are), but one, in which some of the atoms are still in the neighbourhood of their former molecule-partners. Thus, in addition to the " normal " probability of recombination governed by the law of mass-action there will be an additional probability of " primary recombination " of two particles which have been parts of the same molecule before dissociation. When two radicals meet again in the course of their diffusion, the probability of recombination will not, as in the dissipation-effect, be affected through the excess of energy which they possessed in the moment of dissociation ; the case will be that of ordinary recombination in a triple collision to which an efficiency of 1 is commonly ascribed.

This effect exists principally also in the gaseous state, but can be completely disregarded there. Let A (Fig. 2) be an atom formed through dissociation of a molecule RA. We assume that A has lost all its excess energy in a collision with a third body at a distance λ (mean free path) from R (we disregard in this way the so-called " persistence of velocity ").
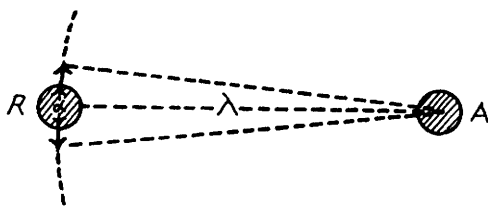
[7] E. Rudberg, *Z. Physik*, **24**, 247, 1924.

The atom A now starts its motion anew with equal probability for every direction. The probability α' of A meeting again the radical R is obviously equal to

$$\alpha' = \frac{\pi d^2}{4\pi\lambda^2} = \left(\frac{d}{2\lambda}\right)^2$$

where d denotes the molecular diameter [8] (we put it the same for R and A and disregard the difference between $1/\lambda^2$ and $\overline{1/\lambda^2}$). In a gas of atmospheric pressure, λ is of the order 1×10^{-5}; d can be put equal to 3×10^{-8}. It follows

$$\alpha' \simeq 2 \cdot 5 \times 10^{-6}.$$

Since only every 10^{-3}th collision is a triple collision at atmospheric pressure which can thus lead to a recombination, the resulting probability α of the effect in which we are interested is under these conditions only of the order of $2 \cdot 5 \times 10^{-9}$. This probability grows with the third power of the pressure (the mean free path varying with $1/p$ and the probability of a triple collision with p). It will be of the order of 10^{-6} at 10 atm., of 10^{-3} at 100 atm. and of 1 at 1000 atm.—if one could operate with elementary notations of gas kinetics at densities where the mean free path is of the same order as the diameter of the molecules. This estimation is intended only to show that the probability of primary recombination in a condensed system cannot be disregarded; it seems reasonable to expect an effect of this kind reaching the order of 0·1.

Together with the "dissipation-effect" the "primary recombination" *must* affect the quantum yield of photochemical reactions in liquids in so far as they really go through the intermediary of free unsaturated particles and do not use one of the two ways pointed out on page 122, which do not involve a dissociation into two atoms or radicals.

The quantitative efficiency of the two effects considered above must depend on the nature of the dissociation-products [9] and of the solvent (*e.g.*, on its viscosity, etc.) as well as on the absorbed wave-length. In particular, the recombination-effect will probably show a wave-length dependence, decreasing with the increasing energy of the absorbed quantum. A greater excess-energy will permit the dissociation products to find their way through the surrounding " walls " of the solvent and to put more molecular layers between them before coming to rest.

A wave-length effect of this kind has been observed in many photochemical reactions in solutions and explained with different hypotheses constructed *ad hoc*.[10]

The majority of the photochemical reactions studied thus far are much too complicated to provide clear evidence of the connection

[8] The same value of α can be obtained through the consideration that α must be equal to the proportion $N_d/N_{2\lambda}$, where N_d means the number of collisions in a gas with the molecular diameter d and $N_{2\lambda}$ the same number in an imagined gas with a molecular diameter 2λ.

[9] The existence of the least energy-barrier for the recombination will cause the primary recombination effect to disappear. Thus no danger of primary recombination exists in the case of a dissociatien into an atom (or radical) and a molecule, *e.g.* of Cl_2O into Cl_2 and O, since all reactions between atoms and molecules seem to need a certain amount of activation-energy.

[10] See for instance the work of E. Warburg, Rump, *Z. Physik*, **47**, 305, 1928, **58**, 291, 1929; *Berl. Akad. Ber.*, **1918**, 1928, on the dissociation of HI and H_2S and the reduction of NO_3' in solution, or of Ogg, Leighton, and Bergstrom (*J. Amer. Chem. Soc.*, **55**, 1754, 1933) on the formation of amids in metal-solutions in liquid ammonia.
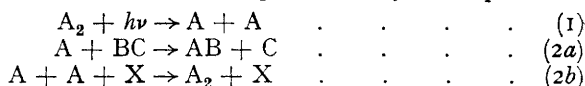
between the observed wave-length-effects and the primary recombination of dissociation-products. We intend to study this question on the simplest possible examples; *e.g.*, through direct investigation of the stationary concentration of free atoms in a solution of iodine in CCl_4 when strongly illuminated with light of different wave-lengths.

III. Secondary Recombination and the Temperature-Coefficient.

The equilibrium concentration of free atoms or radicals in a solution, as compared with a gas, is affected not only by a decreased rate of formation and the possibility of " primary recombination " but also by an increased probability of " normal " or " secondary " recombination, resulting from the fact that every collision of two radicals or atoms in solution is made a " triple " or " multiple " collision by the presence of the molecules of the solvent. Thus the velocity of normal recombination will in every solution be greater by the factor 10^3 to 10^4 than it is in a gas at atmospheric pressure.

We have seen that the " primary " recombination-effect may account for the characteristic influence of wave-length on the quantum-yield of some photochemical reactions in solutions. We shall show that the " secondary " recombination may in some cases provide an explanation for other peculiar properties of photochemical reactions in liquid phases —for their dependence on concentration and their relatively high temperature-coefficients.

Let us consider a chemical reaction represented by the equations:

$$A_2 + h\nu \rightarrow A + A \qquad . \qquad . \qquad . \qquad . \qquad (1)$$
$$A + BC \rightarrow AB + C \qquad . \qquad . \qquad . \qquad . \qquad (2a)$$
$$A + A + X \rightarrow A_2 + X \qquad . \qquad . \qquad . \qquad . \qquad (2b)$$

This is a fairly general scheme of a photochemical reaction proceeding through the intermediary of free atoms, with a quantum yield depending on the competition between the substitution $(2a)$ and the normal recombination $(2b)$. If the reaction $(2a)$ should have no or but a small energy of activation, then $(2b)$ will play no rôle at all in the mechanism of the reaction, since the " acceptor " BC is normally present in a concentration which is many orders of magnitude greater than the equilibrium-concentration of free atoms A at any practically obtainable intensity of illumination. The quantum yield will be that of the reaction (1), independent of temperature or concentration of the acceptor. One can easily calculate, how high the activation-energy of $(2a)$ must be in order that the influence of temperature becomes measurable.

For the velocity v of the formation and the disappearance of the atoms A we have the equations :

$$+ \frac{d[A]}{dt} = 2N \qquad \begin{array}{l} (N = \text{number of absorbed quanta} \\ \text{pro sec. and cm.}^3) \end{array}$$

$$- \frac{d[A]}{dt} = c_1[A]^2 + c_2[A][BC]e^{-Q/RT}.$$

(The use of the simple Arrhenius' expression $e^{-Q/RT}$, where Q is the activation-energy of the reaction $(2a)$ may be permitted in a rough estimation.)

$$c_1[A]^2 + c_2[A][BC]e^{-Q/RT} - 2N = 0 \quad \text{(stationary state)}.$$

$$[A] = -\frac{c_2}{2c_1}[BC]e^{-Q/RT} + \sqrt{\left[\frac{c_2[BC]e^{-Q/RT}}{2c_1}\right]^2 + \frac{2N}{c_1}}.$$

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For the reaction-velocity v we obtain:

$$v = -\frac{d[A_2]}{dt} = \tfrac{1}{2}c_2[A][BC]e^{-Q/RT}$$

$$= \frac{c_2{}^2[BC]^2}{4c_1}e^{-2Q/RT}\left(\sqrt{1 + \frac{8c_1Ne^{2Q/RT}}{c_2{}^2[BC]^2}} - 1\right) \quad . \quad . \quad (3)$$

The absolute value of v (and of the quantum yield $\gamma = v/N$) depends on the value of $C = (8c_1Ne^{2Q/RT})/(c_2{}^2[BC]^2)$. If the conditions are such that $C \gg 1$, and also $\sqrt{C} \gg 1$ (an intense illumination, or a high activation-energy, or a low concentration of the acceptor), then from (3) we deduce:

$$v \ll 2N,$$
and $$\gamma \ll 1.$$

In the other extreme case, $C \ll 1$, we obtain (with the use of the development $\sqrt{1 + \alpha} \simeq 1 + \alpha/2 + \ldots$)

$$v = N,$$
and $$\gamma = 1.$$

In using the same development we can demonstrate that the velocity v becomes markedly affected by temperature as soon as C ceases to be small in comparison with 1. The condition to be satisfied for the temperature-coefficient becoming greater than 1 is thus:

$$e^{2Q_m/RT} \simeq \frac{c_2{}^2[BC]^2}{8Nc_1}.$$

Suppose that reaction (2a) occurs at every collision in which the energy Q is present; and reaction (2b) at every triple collision. Then we have $c_1 \simeq \alpha \times 10^{-9}$ and $c_2 = 0.5 \times 10^{-9}$, where α denotes the probability of a collision being a triple collision (the concentrations are measured in numbers of molecules in ccm.). We choose as example the values $N = 0.5 \times 10^{16}$ for the intensity of absorption and $[BC] = 10^{19}$ for the concentration of the acceptor (corresponding to a gas at $\tfrac{1}{3}$ atm. or to a 0.016 N solution).

The right side of the last equation is, under these conditions, of the order of $6 \times 10^{11}/\alpha$. In the case of a gas at $\tfrac{1}{3}$ atm. α is of the order of 10^{-4}; in the case of a solution of the order of 1. It follows

$$e^{2Q_m/RT} \simeq 6 \times 10^{11} \text{ for solution,}$$
or $$\simeq 6 \times 10^{15} \text{ for a gas,}$$

and, at $T = 300°$ abs.

$$Q_m \simeq 8.3 \text{ Cal. for solution,}$$
or $$11.0 \text{ Cal. for a gas.}$$

So long the activation-energy does not attain these values the reaction as a whole will show no dependence on temperature at all.

If C is not only ≥ 1, but $\gg 1$, and also $\sqrt{C} \gg 1$, then the formula for the reaction-velocity becomes

$$v = \frac{c_2[BC]}{\sqrt{2c_1N}}e^{-Q/RT} \quad . \qquad . \qquad . \qquad . \quad (4)$$

and the dependence on temperature is governed by the ordinary Arrhenius law. In this limiting case the dissociation (1) and the recombination (2b) are both swift in comparison with the substitution (2a), and only a small part of the free atoms disappears by way of reaction. This case is analogous to the ordinary thermal activation, where the activation and deactivation are also assumed to be swift processes in comparison with the reaction itself.
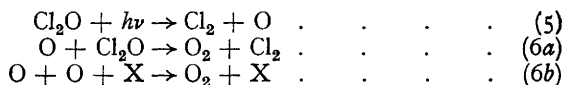
We make again the same assumption as to N, [BC], c_1, and c_2 as above. The condition $\sqrt{C} \gg 1$ will be satisfied, if $\log C \geq 2$. In admitting this value of $\log C$ we obtain from (4)

$$Q \simeq 12 \cdot 6 \text{ Cal. with } \alpha = 10^{-4} \text{ (gas)}$$

or $\qquad Q \simeq 10 \cdot 8 \text{ Cal. with } \alpha = 1 \text{ (solution).}$

Thus, under the accepted conditions, there will be no temperature influence on the quantum yield with Q below $8 \cdot 3$ Cal. in solution or $11 \cdot 0$ Cal. in gas; and a "full" temperature-coefficient above $Q = 10 \cdot 8$ Cal. in solution or $12 \cdot 6$ Cal. in gas (the same variation of Q will decrease the absolute quantum yield from 1 to 0). In the transition-region the temperature-coefficient will be very sensitive against concentration and light-intensity. Since the activation-energies of reactions of free atoms with molecules have been found to be of the order of 5 to 10 Cal. it is not impossible that in some cases the observed relatively high temperature-coefficients of photochemical reactions in solutions may be explained in this way. It is not impossible that in a special case going over from a reaction in a gas to the same reaction in solution, one would pass from the limiting conditions permitting a full quantum-yield without appreciable temperature-coefficient to conditions yielding an extremely small quantum-efficiency coupled with a high temperature-coefficient. Both quantum yield and temperature-coefficients will generally depend on light intensity and concentration.

As a matter of fact, in many investigations of photochemical processes in the liquid state high temperature-coefficients have been found, together with a small quantum yield and strong dependance on concentration and light intensity. In our opinion, such results point to an "atomic" mechanism of these reactions and to an activation energy of the order of 10 Cal. for the "stabilising" reaction. There exist some reactions in which the quantum yield $\gamma = 2$ has been found in gases and $\gamma \simeq 1$ in solutions, e.g., the dissociation of Cl_2O.[11] We can suppose, that the mechanism of this reaction is:

$$Cl_2O + h\nu \rightarrow Cl_2 + O \qquad . \qquad . \qquad . \qquad . \qquad (5)$$
$$O + Cl_2O \rightarrow O_2 + Cl_2 \qquad . \qquad . \qquad . \qquad (6a)$$
$$O + O + X \rightarrow O_2 + X \qquad . \qquad . \qquad . \qquad (6b)$$

The process (5) gives in gas the quantum yield $\gamma = 1$ and will not be strongly affected through the presence of a solvent because one of the dissociation products is a saturated molecule. The process (6a) and (6b) provide an example of a competition between substitution and secondary recombination discussed above; and it is not improbable that (6a) will be predominant in a gas, thus giving a resulting quantum yield $\gamma = 2$, but will practically disappear in solution.

Unfortunately, there are few thoroughly studied examples of

[11] Bowen, *J. chem. Soc.*, **123**, 1199, 2238, 1923; Bodenstein, Kistiakowsky *Z. physik. Chem.*, **116**, 371, 1925.

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reactions in liquids on which the considerations here discussed can be applied.   Even the example of Cl_2O is not quite reliable, since the results of previous investigations have been questioned in a later work.[12] On this point also it would be useful to initiate experimental work on the simplest photochemical reactions that can be studied in gaseous and in liquid phases under the same conditions of concentration and temperature.