

THE CHEMISTRY OF SOME PHOTOREACTIONS IN NON-IDEAL SOLUTIONS

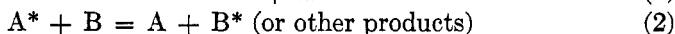
G. K. ROLLEFSON

Department of Chemistry, University of California, Berkeley, California

Received October 14, 1935

Modern photochemistry has rather neglected the subject of reactions in solutions, particularly solutions in which the dissolved molecules are markedly affected by the solvent. The latter type is the one I have chosen to call non-ideal solutions, and I wish to discuss those reactions in which the light-sensitive molecule undergoes no net change, i.e., sensitized reactions. The sensitizing molecule may (1) transfer its energy after activation to another molecule by a collision of the second kind, (2) form a complex ion or molecule with one of the reactants, this complex acting as the effective light absorber, or (3) enter into a series of reactions leading to the net reaction for the system with regeneration of the sensitizer. The first of these possibilities has been the most popular in the literature, one of the most general discussions being that of Franck and Levi (2). The paucity of literature concerning the other two types of sensitizing action is probably due in part to the experimental difficulties involved in obtaining exact information concerning the substances involved (such as complex ions or intermediates at low concentrations), and in part to a tendency to accept the collision-of-the-second-kind hypothesis on account of its apparent simplicity. In this paper I wish to discuss some reactions from the standpoint of the classification given above, in order to show what experiments are needed to determine the true mechanisms.

The particular reactions to be considered are some involving the uranyl ion or dyes such as eosin, so that we are dealing with systems in which the primary action of the light is to produce an activated molecule. If we assume that this photoactivated molecule, A^* , transfers its energy to some other molecule, B , by a collision of the second kind, thus bringing about a reaction, then we have a competition which may be represented by the equations



This leads to the law $-d(B)/dt = I_{\text{abs.}} (1/[1 + k_1/k_2(B)])$, if we assume that any steps occurring after equation 2 are not rate-determining. If

the reaction is a more complex one, this rate law will be multiplied by some function of the concentrations. It is to be noted, however, that this law is not specific for processes such as we have included in equations 1 and 2, but may be derived for many other processes, as, for example, any competition between a unimolecular and a bimolecular process. As a rule other complications enter, so that the agreement between this rate law and the experimental results is qualitative rather than quantitative. In order to discuss these complications we must deal with particular reactions.

As our first example let us consider the decomposition of oxalic acid sensitized by uranyl salts. West, Muller, and Jette (7) and also Pierce (5) have attempted to interpret the behavior of this system by assuming that the absorption of light produced activated uranyl ions which transferred their energy to the oxalic acid molecules, causing a decomposition. Such an interpretation encounters several difficulties. First, the absorption of the effective wave lengths by the solution is increased markedly (approaching a definite limit) on the addition of oxalic acid, a fact which is not accounted for quantitatively in this simple theory. Second, the uranium must be considered as present in at least two molecular species, such as the undissociated salt and its ions or two ions containing uranium.¹ This leads to complications in applying the simple law deduced from equations 1 and 2. If we assume that only one molecular species is effective in producing reaction, then the factor $I_{\text{abs.}}$ must be modified so as to represent the light absorbed by that molecule alone. If we assume that all of the activated uranyl compounds are effective, then we must consider that k_1 and k_2 are probably not the same for all the substances, and therefore the experimental results should not fit a simple law such as we have given, but should fit one containing two or more terms, each of which is of that form. It is therefore possible to set up an equation which will take account of the various molecules which contain the sensitizer, but this has not been done by the advocates of this mechanism.

If we adopt the second type of mechanism, the formation of a complex between uranyl ion and some form of oxalate as suggested by Leighton and Forbes (3), the increase in absorption on adding oxalate can be accounted for by assuming that the absorption coefficient is higher for the complex than for the uranyl ion. McGinnis (4) has compared the change in the rate of decomposition of the oxalate over a range of 0.01 to 2 molal hydrogen-ion concentration with the change in absorption over the same range, and concluded that the results could be explained by assuming

¹ This conclusion is based on a consideration of conductance measurements by Dittrich (1), which show that while uranyl salts conduct so well that a considerable amount of ionization must be assumed, the ionization is by no means complete at the concentrations used in photochemical experiments.

that the uranium was present as UO_2^{++} , $\text{UO}_2\text{HC}_2\text{O}_4^+$, and UO_2OH^+ , but only the light absorbed by the $\text{UO}_2\text{HC}_2\text{O}_4^+$ was effective in causing decomposition of the oxalate. It follows that the most simple mechanism involves the decomposition of this complex, but the data available do not permit a decision as to whether the final products are obtained immediately or some other intermediates are formed first. One possibility would be that carbon dioxide splits out, leaving a uranyl formate complex which breaks up on the absorption of another quantum of light. Such a process would be useful in accounting for the low quantum yield (approximately 0.6), and might explain the variation in quantum yield with wave length, which was studied in some detail by Leighton and Forbes. Small amounts of formate are actually found in the solution after the reaction has proceeded to a considerable extent, but this cannot be considered very significant unless it is shown that the uranyl formate complex has a photochemical decomposition rate so much higher than the oxalate complex that only small amounts of formate could remain in solution. In order to test these possibilities it is necessary to have measurements of the absorption coefficients and rates of decomposition of uranyl formate solutions for a number of wave lengths of light. This combination of two successive reactions may be considered as a simple example of the third type of mechanism.

Turning to the subject of sensitized photooxidations by dissolved oxygen, we find many more possibilities than for the reaction we have just considered. Even in applying the collision-of-the-second-kind hypothesis we find two different viewpoints expressed in the literature. One advocates a transfer of energy from the activated sensitizer to the oxygen molecule changing it to the $^1\Sigma$ state, which is assumed to be more reactive than the normal state of the oxygen molecule. The other considers that the energy is transferred to the substance to be oxidized, putting it into a form more susceptible to the action of the oxygen. The latter seems to be the more reasonable assumption, as these oxidations can be brought about by visible light, and there is no reason to believe that any state of the oxygen molecule which can be reached with the aid of such energies is any more reactive than the normal state. A particular example of the application of this theory is found in the recently published work of Schneider (6) on the oxidation of iodide sensitized by uranyl compounds, fluorescein, rhodamine, and quinine bisulfate. His results are in qualitative agreement with the theory, especially in that the long-lived active state of the uranyl compounds is much more effective at low iodide concentrations than the shorter-lived states of the other molecules. This fact alone, however, is not enough to warrant the exclusion of other possible explanations. Schneider's results show many effects which he leaves unexplained, as, for example, the marked influence of acid on the uranyl-sensitized

reaction and the different behavior of lithium and potassium iodides in the same reaction. These are of great importance, as the collision-of-the-second-kind hypothesis requires a simple law as far as the actual reactants are concerned, so these other effects must be explained as due to secondary effects.

The data available at present are not sufficient to establish any of the other possibilities, so we shall just list them briefly, indicating what kind of evidence is needed. The uranyl compounds offer the best opportunity for the application of the "complex" theory, as there is considerable evidence for uranyl compounds being weak electrolytes. If that theory is correct it should be possible to demonstrate that the rate of the reaction is proportional to the amount of complex (or weak electrolyte) present. Such a proof involves a determination of the equilibrium existing in the solution. It is, of course, possible that other factors may influence the rate also in particular reactions, but the most important fact to be fixed for a theory of this kind is the proportionality between the rate and the amount of complex. The amount of complex may be determined by independent methods, such as a study of absorption coefficients, thus giving a check on the conclusions deduced from rates.

The third type of mechanism, the one involving a series of reactions, is extremely adaptable. One possibility which is quite general is that the activated sensitizer forms a peroxide which reacts with the reducing agent. Such a reaction almost certainly enters in the eosin-sensitized oxidations, and this may be a general phenomenon. It is not necessary to show the presence of peroxide in such reactions, unless it can be shown that a detectable amount of peroxide can exist in the solution under the experimental conditions. Another possibility is that the sensitizer may be reduced and then be oxidized by the dissolved oxygen. If the "stationary state" concentration of the reduced form is very low, it would be possible to have this mechanism hold for reducing agents so weak that a blank test in the absence of oxygen would show no reaction. These chemical mechanisms may produce very complicated rate laws, and it may be that the explanation of the failure of the simple collision-of-the-second-kind theory in many reactions is that the actual processes are true chemical reactions rather than merely energy transfers.

In order to arrive at the best solution of these problems the following procedure is suggested:

1. Determination of the formulas and the amounts of the dissolved molecules of the reactants.
2. Determination of the variation of the quantum yield with wave length. This is not a conclusive test but may be of considerable help in that it is known that the transfer of energy is most efficient

when it is the exact amount which can be utilized by the receiving molecule (8). Thus in a reaction involving collisions of the second kind we should expect to find the quantum yield a maximum near the long wave length limit and decreasing toward shorter wave lengths.

3. Determination, quantitatively, of the effect of altering the concentration of each substance present in the solution, including hydrogen ion.

With complete information available all the possible theories could be tested, and it would not be surprising if we found examples of all three types.

REFERENCES

- (1) DITTRICH: *Z. physik. Chem.* **29**, 469 (1899).
- (2) FRANCK AND LEVI: *Z. physik. Chem.* **27B**, 409 (1935).
- (3) LEIGHTON AND FORBES: *J. Am. Chem. Soc.* **51**, 3139 (1930).
- (4) MCGINNIS: Thesis, University of California, 1935.
- (5) PIERCE: *J. Am. Chem. Soc.* **51**, 2731 (1929).
- (6) SCHNEIDER: *Z. physik. Chem.* **28B**, 311 (1935).
- (7) WEST, MULLER, AND JETTE: *Proc. Roy. Soc. London* **121A**, 294 (1928).
- (8) ZEMANSKY: *Phys. Rev.* **36**, 919 (1930).

DISCUSSION

DR. W. G. LEIGHTON (Pomona College): Professor Rollefson has suggested the possibility that the quantum yield in the uranyl oxalate photolysis ($\Phi = \text{ca. } 0.6$) is less than unity because of absorption by uranyl formate, itself produced in the reaction. If such absorption is a significant factor, both a decrease in quantum yield and an increase in absorption should be observed through the early stages of photolysis, as the formate begins to accumulate. Bearing on this it is recalled that, in a series of some fourteen determinations of quantum yield at λ 366 m μ reported with Forbes, we found no systematic change in either the yield or the absorption coefficient over the range 2 per cent to 16 per cent oxalic acid decomposed. These results were obtained with a solution containing initially five moles of oxalic acid to one of uranyl sulfate.

The low quantum yield in uranyl oxalate might be accounted for through recombination of photochemical products, or again, through deactivation of excited uranyl oxalate complex by water molecules. Similarly, the inhibitory effect of Cl^- , Br^- , SCN^- , and I^- could possibly be interpreted as due to deactivation of the excited complex by these ions, although the complex-forming tendencies of these ions should not be overlooked.

In support of the "complex" theory as applied to the uranyl oxalate photolysis, it seems appropriate to present certain data which we have

used in attempting to apportion the energy absorbed in this system. The curve in figure 1, like one described by Ghosh and Mitra, shows the striking increment in absorption coefficient when oxalic acid is added to a fixed concentration of uranyl sulfate. As plotted, none of the increase is due to absorption by the oxalic acid itself, as correction was made for this contribution (nearly negligible at λ 313 $m\mu$). The curve is just what would be expected if a strongly absorbing complex is formed, or perhaps an equilibrium mixture of such compounds. If a single complex predominates under the experimental conditions, its absorption coefficient should correspond approximately to the limit approached by the curve. Along the

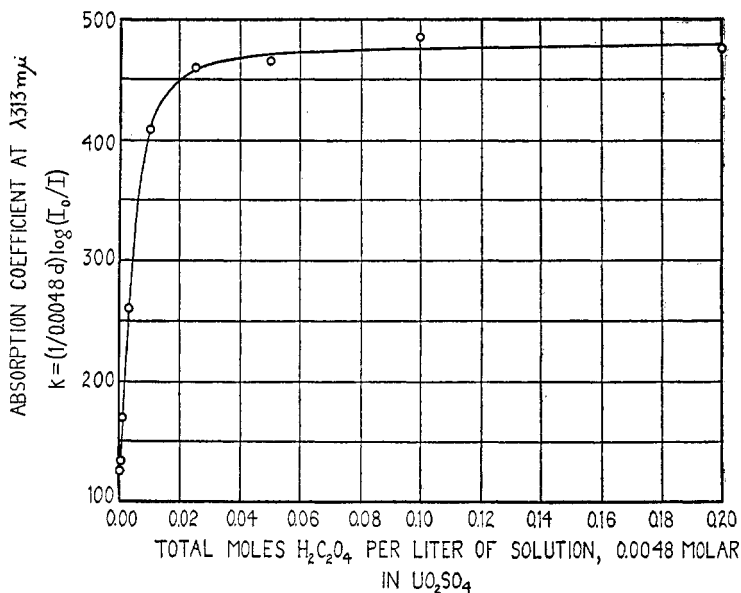


FIG. 1

steep part of the curve the equilibrium concentrations could then be calculated, as was done by Ghosh and Mitra, from the equation

$$\log \left(\frac{I_0}{I} \right)_{\text{observed}} = \sum kc = k_{\text{UO}_2\text{SO}_4} \cdot ([\text{UO}_2\text{SO}_4, \text{total}] - [\text{complex}]) + k_{\text{complex}} \cdot [\text{complex}]$$

Equilibrium concentrations calculated from the experimental curve by means of this equation are shown in table 1. In the last column the stability constant of the complex is calculated, assuming that the predominating complex contains one oxalate and one uranyl group. The constancy obtained is perhaps as good as could be expected, considering the fact that

both the effect of hydrogen ion on the equilibrium and also the possible presence of a higher complex were disregarded. A similar calculation assuming the predominating complex to contain two oxalates with one uranyl group gave values for the stability constant ranging from $K = 5 \times 10^4$ in a 1:5 mixture to $K = 70 \times 10^4$ in a 1:2 mixture, becoming infinite at somewhat lower excess of oxalic acid. Apparently the former

TABLE 1

Equilibrium concentrations and stability constant of the uranyl oxalate complex

TOTAL MOLES PER LITER		$k_{\text{obsd.}}^*$	EQUILIBRIUM CONCENTRATIONS			STABILITY CONSTANT
UO_2SO_4 u	$\text{H}_2\text{C}_2\text{O}_4$ a		UO_2SO_4 $u - X$	$\text{H}_2\text{C}_2\text{O}_4$ $a - X$	" $\text{UO}_2\text{C}_2\text{O}_4$ " X	$\frac{X}{(u - X)(a - X)}$
0.0048	0.1-0.2	2.31±	0.0000	0.1-0.2	0.0048	
0.0048	0.0000	0.60	0.0048	0.0000	0.0000	
0.0048	0.0250	2.20	0.0003	0.0205	0.0045	7×10^2
0.0048	0.0100	1.96	0.0010	0.0062	0.0038	6×10^2
0.0048	0.0030	1.25	0.0030	0.0012	0.0018	5×10^2
0.0048	0.0010	0.81	0.0042	0.0004	0.0006	4×10^2

* $\lambda 313 \text{ m}\mu$ (corrected for absorption by excess oxalic acid).

TABLE 2

Quantum yield referred to the uranyl oxalate complex

MOLES PER LITER			RELATIVE ABSORPTION BY COMPLEX† AT $\lambda 313 \text{ m}\mu$	QUANTUM YIELD AT $\lambda 313 \text{ m}\mu$	
Total		Equilibrium*		Gross	Referred to complex
UO_2SO_4 u	$\text{H}_2\text{C}_2\text{O}_4$ a	" $\text{UO}_2\text{C}_2\text{O}_4$ " X	$\frac{k_x X}{\Sigma kc}$	Φ_g	$\Phi_g \cdot \frac{\Sigma kc}{k_x X}$
0.001	0.050	0.0009(7)	0.98	0.57(7)	0.59
0.010	0.050	0.0096	0.99	0.56(1)	0.57
0.020	0.040	0.0186	0.98	0.55(5)	0.57
0.010	0.010	0.0067	0.89	0.51(5)	0.58

* X follows from the stability constant, $K = 6 \times 10^2$ (table 1).

† $k_u = 125$, $k_x = 480$, $k_a = 0.2$; $\Sigma kc = k_u(u - X) + k_x X + k_a(a - X)$.

assumption, as illustrated in table 1, is more nearly correct in the case of the mixtures studied. To be sure this conclusion does not distinguish between such possibilities as $\text{UO}_2\text{C}_2\text{O}_4$ and $\text{UO}_2\text{HC}_2\text{O}_4^+$, etc. This question now seems to be answered in favor of $\text{UO}_2\text{HC}_2\text{O}_4^+$, according to Professor Rollefson.

In table 2 the equilibrium concentration and relative absorption of the

complex are approximated from the average stability constant ($K = 6 \times 10^2$) for several mixtures in the case of which the quantum yield was also determined. It is interesting to note that absorption by the complex accounts for 99 per cent of the total absorption in a 1:5 mixture at λ 313 $m\mu$, while even in a 1:1 mixture the complex receives nearly 90 per cent of the total light absorbed. Supporters of the theory that energy is transferred from excited UO_2^{++} to oxalic acid molecules by collisions of the second kind, must reckon with the quantitative fact that the absorption by UO_2^{++} in mixtures containing excess oxalic acid is so small as to be without significance, unless yields of the order of 25 to 75 are postulated. In the last column of table 2 the calculations of relative absorption by the complex are applied to correct the quantum yield to the basis of light absorbed by the complex alone. The improved constancy thus obtained over a wide range of concentrations agrees with the view that the initial photochemical process consists in the direct excitation of complex followed by decomposition. If one prefers, this may be stated that the rate of photolysis is proportional to the light absorbed by the complex, in agreement with the findings of Rollefson and McGinnis.

PROFESSOR R. LIVINGSTON (University of Minnesota): The following preliminary experimental results may be of interest in connection with the discussion of the mechanism of the decomposition of oxalic acid sensitized by uranyl ion. The hypothesis of West, Muller, and Jette suggests that any ion which is fluorescent in solution may be capable of acting as a sensitizer. Since samarium salts have been reported to be fluorescent in solution we have begun an investigation of their sensitizing action. A saturated solution of samarium oxalate in 0.05 *N* sulfuric acid was exposed to the radiation of a quartz mercury arc through a corex D filter for periods as long as two hours. Under these conditions there was no detectable sensitized decomposition, although when uranyl oxalate was substituted for the samarium salt (under the same conditions of concentration and intensity) about 60 per cent of the oxalic acid was decomposed in twenty minutes.