At 109°, the rate constant for alcoholysis catalyzed by p-toluenesulfonic acid is about one-eleventh of that for esterification. The difference, 1000 cal., between the activation energies[10] is greater than the experimental error (about ± 300 cal. in each case). This difference is sufficient to account for a 3.7-fold difference in the rates at 109°. Since the ratio of the rates is greater than this factor, the entropy of activation for the esterification reaction probably is slightly greater than that for alcoholysis.

Catalysis by Carboxylic Acid.—In expt. 3 of the preceding paper the viscosity of a mixture of polyester B and decamethylene glycol decreased very slowly in complete absence of p-toluenesulfonic acid catalyst. This process has been attributed to catalysis by the free carboxyl groups present in polymer B at a concentration of 3.4×10^{-2} mmol./g. The rate of viscosity decrease was about one-eightieth of the initial rate observed in expt. 8 in which the p-toluenesulfonic acid concentration was 0.45×10^{-2} mmol./g.; glycol concentrations were about the same in each experiment. Hence the carboxylic acid end-

groups are about one six-hundredth as effective as p-toluenesulfonic acid catalyst; for carboxyl group catalyzed alcoholysis at 109°, $k \cong 4 \times 10^{-4}$ (mmol./g.)$^{-2}$ min.$^{-1}$. Approximate evaluation of the rate of alcoholysis from the viscosity decrease when a low and a high molecular weight polyester are mixed (without adding a catalyst) yields a similar value, 6×10^{-4}, for k.[11]

Unpublished results on rates of polyesterification of decamethylene glycol and adipic acid catalyzed by carboxyl groups yield $k \cong 5 \times 10^{-4}$ (mmol./g.)$^{-2}$ min.$^{-1}$ at 109°. Thus, when carboxylic acid is the catalyst, the rates of esterification and alcoholysis appear to be about the same. Compared with p-toluenesulfonic acid, carboxylic acid appears to be relatively less effective as an esterification catalyst than as an alcoholysis catalyst. This difference between these similar reactions should be investigated further.

Summary

Rates of polyesterification and of alcoholysis of polyesters have been measured by viscosity methods. When p-toluenesulfonic acid is the catalyst at 109°, the rate constant for esterification is about eleven times that for alcoholysis. The activation energies are 12,150 and 11,150 cal., respectively. Preliminary experiments indicate that esterification and alcoholysis rate constants are about the same when carboxylic acid is the catalyst.

(10) W. A. Waters, *J. Chem. Soc.*, 1014 (1936), has shown that the rates of hydrolysis and alcoholysis of phenyl benzoate in ethanol-water mixtures are approximately equal. The activation energies (16,500 cal.), though larger than we have observed for an aliphatic ester, are approximately the same within the experimental error (± 1000 cal.). Since esterification reactions ordinarily are approximately thermally neutral, the activation energy for the formation of phenyl benzoate probably is about equal to that for its hydrolysis. It follows that activation energies for the formation and for the alcoholysis of this ester must be about the same, in harmony with the results reported here.

(11) This estimation of k is based on results of the sort shown in Fig. 6 of ref. 5.

The Quenching of Fluorescence in Solution. II. Temperature and Solvent Effects

BY R. W. STOUGHTON AND G. K. ROLLEFSON

In a previous paper[1] we have shown that the quenching of fluorescence in solution is influenced by ionic strength in the same way as an ordinary bimolecular reaction involving ions. The quenching process may be considered therefore as a relatively simple bimolecular reaction which is readily followed by studying the rate of disappearance of one of the reactants, i. e., the photoactivated molecule. In this paper we wish to present some observations on the effect of changes in the nature of the solvent and of temperature on reactions of this kind.

If we consider the specific reaction rate of a bimolecular reaction as composed of two factors of which one depends on the activation energy and the other is proportional to the number of collisions, it is the latter which may be expected to be dependent on the viscosity of the solvent. Any calculation of the effect of viscosity on the collision number requires assumptions such as that the apparent viscosity of the solvent to a molecule is the same as the macroscopic value. Ölander[2] concluded that the collision number and hence the specific reaction rate should be inversely pro-

(1) Stoughton and Rollefson, THIS JOURNAL, **61**, 2634 (1939).

(2) Ölander, *Z. physik. Chem.*, **A144**, 118 (1929).

portional to the viscosity. Eyring[3] has discussed diffusion processes in liquids and has reached the conclusion that the diffusion rate should be inversely proportional to the viscosity with some modifications dependent on the relative sizes of the solute and solvent molecules. The rate of a bimolecular reaction should vary the same as the diffusion rate. In order to obtain experimental evidence on this point we have varied the viscosity by varying the temperature and also by varying the composition of the solvent.

The fluorescent substances used in these experiments were quinine sulfate, fluorescein, and acridone. The quenchers were potassium chloride and iodide. These substances were the same as were used in the work previously described. The solvents other than water were glycol, glycerol, methyl alcohol and mixtures of these with water. The glycol was vacuum distilled. The glycerol was heated to 180° for half an hour to remove most of the water since there was no other impurity present in appreciable quantities. The apparatus used in making the measurements was the same as described in the previous paper.

The ideal procedure to follow in the study of viscosity effects would be to compare k_0 for solutions of various viscosities. Practically, this cannot be done satisfactorily since k_0 must be obtained by extrapolation and especially in the more viscous solutions this extrapolation must be carried over such a long range that the resulting values are not very accurate. Therefore we have followed the procedure of determining the quenching caused by a definite concentration of quencher in solutions of various viscosities. The results have been expressed in terms of the quenching constant and are tabulated in Tables I to VI. The values of k in Tables IV, V and VI are the same as k_0 since the reactions involve a neutral molecule and an ion and in such a case k is not dependent on ionic strength. The data in the other three tables are for reactions in which both reactants are ions and in such cases as we have shown the quenching constant is a function of the ionic strength. The magnitude of the change of the constant due to ionic strength is dependent on both the temperature and the dielectric constant of the solvent. Therefore in the experiments tabulated in Tables I, II and III there is some effect due to changes of temperature and dielectric constant superimposed on the viscosity

(3) Eyring. *J. Chem. Phys.*, **4**, 283 (1936).

effect. These effects are, however, of secondary importance compared to the viscosity effect. This fact is evident from an inspection of Tables I and II. The dielectric constant and temperature effects are in opposite directions in these two systems, as we shall show later in this paper, yet the net change in k is in the same direction and approximately the same percentage for both. Figure 1 is a graphical presentation of the data in Table IV. This is a typical example of the type of curve obtained by plotting k against the reciprocal of the viscosity. Some of the other curves are more linear, others somewhat less, but it seems justi-

TABLE I

QUENCHING OF QUININE SULFATE ($c = 5 \times 10^{-5}$ M) BY 0.005 M KCl IN WATER

t, °C.	η	I_0/I	k
0	0.018	1.465	93
10	.013	1.53	106
25	.0089	1.74	148
40	.0066	1.91	182
55	.0051	2.18	236
70	.0041	2.32	264

TABLE II

QUENCHING OF FLUORESCEIN ($c = 5 \times 10^{-5}$ M) IN 0.001 M KOH BY 0.05 M KI IN WATER

t. °C.	η	I_0/I	k
0	0.018	1.34	6.8
10	.013	1.44	8.8
25	.0089	1.52	10.4
40	.0066	1.62	12.4
55	.0051	1.66	13.2
70	.0041	1.72	14.4

TABLE III

QUENCHING OF FLUORESCEIN ($c = 5 \times 10^{-5}$ M) IN 0.001 M KOH BY 0.8 M KI IN MIXED SOLVENTS AT 25°

Vol. % glycerol	η	I_0/I	k
0	0.0089	18.2	22
16	.0146	12.7	14.6
25	.0201	9.8	11.0
50	.060	4.52	4.4
100	5.0	1.24	0.3
Vol. % glycol			
25	0.0173	9.2	10.3
50	.0346	3.95	3.7
100	.161	1.69	0.86
Vol. % methyl alcohol			
50	0.0153	5.4	5.5

TABLE IV

QUENCHING OF ACRIDONE BY 0.01 M KI IN WATER

t, °C.	η	I_0/I	k
0	0.018	1.55	55
25	.0089	1.84	84
45	.0060	2.15	114
60	.0047	2.42	142
75	.0038	2.62	162

TABLE V

QUENCHING OF ACRIDONE BY 0.2 M KI IN GLYCEROL

t. °C.	η	I_0/I	k
3	40	1.09	0.45
25	5	1.20	1.0
45	1.4	1.50	2.5
72	0.33	2.40	7.0

TABLE VI

QUENCHING OF ACRIDONE BY KI IN MIXED SOLVENTS AT 25°

Vol. % glycerol	η	C_{KI}	I_0/I	k
0	0.0089	0.01	1.84	84
16	.0146	.05	3.90	58
25	.0201	.1	5.23	42
50	.060	.1	2.80	18
75	.33	.1	1.57	5.7
100	5.0	.2	1.20	1.0
Vol. % glycol				
25	0.0173	0.05	3.50	50
50	.0346	.05	2.33	27

fiable to conclude that rate constants for reactions of the kind we are dealing with are at least qualitatively inversely proportional to the viscosity of the solvent. Only one exception to this rule has been found in our work. The quenching of the fluorescence of quinine sulfate by silver nitrate changes very little between 0 and 60°, although the viscosity changes by a factor of four.
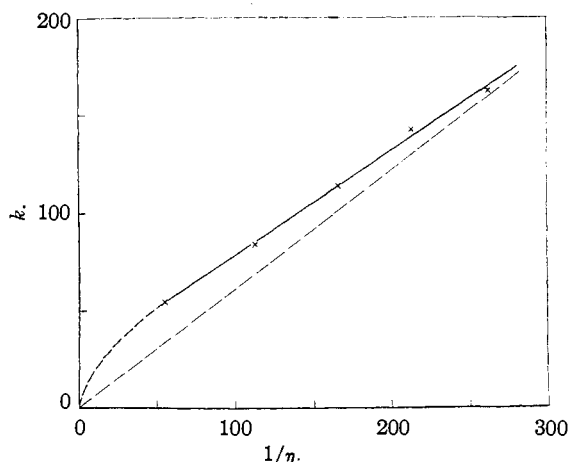

Fig. 1.—Quenching of acridone by potassium iodide at various temperatures in water.

Temperature and Dielectric Constant Effects.— A change of temperature may affect the quenching constant in the following ways: (1) it may change the viscosity, and this effect already has been discussed; (2) it may change the number of collisions between the activated and the quencher molecules; (3) if the quenching process requires activation energy an increase in tem-

perature will increase the number of molecules with the necessary energy; (4) it may alter the effect of ionic strength on the magnitude of the quenching constant. The second and third possibilities are most readily discussed together. If we write the quenching constant as $k = Se^{-Q/RT}$, the second effect corresponds to a change of S and the third to a change of Q. An inspection of the data in Tables I, II, IV and V shows that the change in viscosity with temperature is able to account, at least qualitatively, for all of the change in k. It can be stated definitely that in these cases there can be no appreciable energy of activation for the quenching process. The change in the number of collisions depends on the square root of the temperature. Over the temperature range used in our experiments this amounts to a maximum change of slightly over 10%. Since we do not have an accurate quantitative equation for the viscosity effect, it is impossible to detect this small effect.

The fourth effect of temperature must be discussed together with the dielectric constant effect since both are concerned with the influence of ionic strength on the quenching constant. The limiting law at low ionic strength is given by the Debye–Hückel theory combined with the Brönsted equation for a rate constant as

$$\log k/k_0 = A\Delta Z^2\mu^{1/2} \qquad (1)$$

in which A is a constant for any given temperature and solvent, ΔZ^2 is the difference between the square of the charge of the intermediate complex and the sum of the squares of the charges of the reactant molecules, and μ is the ionic strength. The magnitude of A is given by

$$A = \frac{\epsilon^3}{DkT}\sqrt{\frac{2\pi N}{1000DkT}} \qquad (2)$$

in which ϵ is the electronic charge, D the dielectric constant, T the absolute temperature, k the Boltzmann constant, and N the Avogadro number. In addition to the effect given by these equations there is an effect on k_0 which, for bimolecular reactions such as we are studying, is given by Scatchard[4] as

$$\log k_0 - \log k_0^0 = \frac{\epsilon^2 Z_A Z_B}{2.3kTr}\left(\frac{1}{D^0} - \frac{1}{D}\right) \qquad (3)$$

in which r is the radius of the critical complex, Z_A and Z_B the charges on the reactants, k_0 and D are the limiting k and dielectric constant of the solvent in question and k_0^0 and D^0 are the values for some reference solvent.

(4) Scatchard, Chem. Rev., **10**, 229 (1931).

It is obvious that both of these effects vanish if either of the reactant molecules is uncharged. Hence these effects do not appear in such systems as listed in Tables IV, V, VI which involve the neutral molecule acridone. In the other cases the two effects are combined, i. e., both the limiting law and the k_0 change with conditions. The limiting law slope changes only from 0.48 to 0.55 in aqueous solutions between 0 and 65°, hence any effect due to a change of this factor is small compared to the viscosity effects which have been reported. In fact the changes introduced in this factor by the temperature changes are always small so that they cannot be detected from our data. The effect of dielectric constant, however, can be shown by determining the limiting slope in a solvent of lower dielectric constant than water. A mixture of dioxane and water which is 45% by weight dioxane has a dielectric constant of 38.48. Substituting this number for D in the constant A the limiting law for this mixture at 25° becomes

$$\log \frac{k}{k_0} = 1.5 \Delta Z^2 \mu^{1/2}$$

or to express it in the same form as we used in the previous paper for graphical representation

$$\frac{2}{|\Delta Z^2|} \log k/k_0 = 3.0 \frac{\Delta Z^2}{|\Delta Z^2|} \mu^{1/2} \qquad (4)[5]$$

The limiting slope which should be found in these solutions is three times that for water. In order to test this law data were obtained on the quenching of the fluorescence of quinine sulfate by silver nitrate, potassium chloride, and potassium bromide. The results are shown in Fig. 2 along with the activity coefficient curve for hydrochloric acid in this solvent as calculated from the data of Harned and Morrison[6] by a method used by Harned and Donelson.[7] The value of a indicated for each of the curves has the same significance as in our previous paper, i. e., it is $(2/\Delta Z^2) \log k_0$. The approach to the predicted limiting law is as good as could be expected for the potassium chloride and bromide curves. The curve for silver nitrate is still quite far from the limiting slope at the lowest ionic strengths at which it is possible to measure the quenching. This discrepancy, however, is certainly not greater than

might be expected for solvents of this dielectric constant according to the activity coefficient curves of alkali halides in mixed solvents obtained by Åkerlöf.[8] The large deviation does nevertheless make the magnitude of the limiting slope uncertain, but we can say definitely that it is greater than in water solutions.
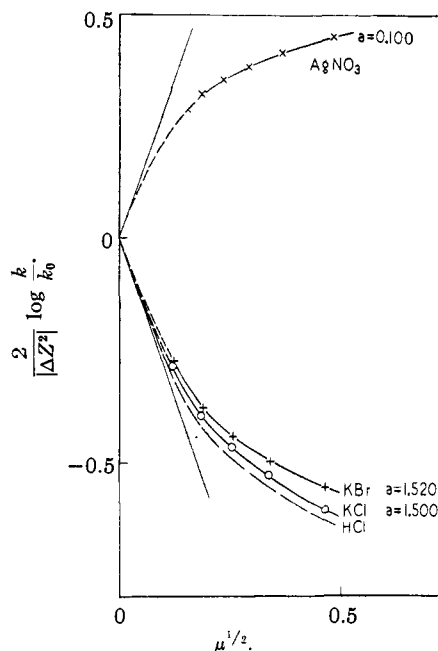

Fig. 2.—Quenching of fluorescence of quinine sulfate by silver nitrate, potassium bromide and potassium chloride in 45% dioxane–water.

The effect of a change in dielectric constant on k_0 is given by equation (3). According to this equation if D^0 is greater than D and Z_A and Z_B are of the same sign, k_0 must be smaller than k_0^0; if Z_A and Z_B are of opposite signs the reverse is true. In a comparison of k_0 for water and water–dioxane mixtures this requires that k_0 in water solution should be larger than that in the water–dioxane solution in the case of the quenching of quinine sulfate by silver nitrate but smaller for the quenching by potassium chloride or potassium bromide. That this statement is qualitatively true is shown by comparison of the a values in these systems. They are shown in Table VII.

TABLE VII

VALUES OF a FOR THE QUENCHING OF QUININE SULFATE IN WATER AND WATER–DIOXANE SOLUTIONS

Solvent	Quencher		
	AgNO$_3$	KCl	KBr
Water	0.202	1.334	1.386
Water–dioxane	.100	1.500	1.520

(5) In the previous paper we neglected to indicate that we divided both sides by the absolute magnitude of ΔZ^2, i. e., $|\Delta Z^2|$. Thus the division on the right-hand side of the equation leaves the sign of ΔZ^2.

(6) Harned and Morrison. THIS JOURNAL, **58**, 1908 (1936).

(7) Harned and Donelson. ibid., **60**, 339 (1938).

(8) Åkerlöf. ibid., **52**, 2353 (1930).

Before any attempt is made to compare the change shown in this table with that called for by equation 3, it is necessary to make a correction for the viscosity effect. The viscosity of the 45% dioxane solution is approximately twice that of water at 25°, hence the comparisons should be made after doubling the value of k_0 in the dioxane–water solution. In Table VIII we have listed the values of log k_0/k_0^0 both before and after making this correction. No correction has been made in the case of quinine sulfate with silver nitrate because of the apparent independence of viscosity already mentioned for that reaction.

TABLE VIII

COMPARISON OF k_0^0 IN WATER SOLUTION WITH k_0 IN 45% DIOXANE–WATER SOLUTIONS

Systems	$Z_A Z_B$	log k_0/k_0^0 Uncorrected	log k_0/k Corrected
Quinine sulfate and KCl	−2	0.33	0.63
Quinine sulfate and KBr	−2	.27	.57
Quinine sulfate and AgNO₃	+2	− .20	− .20
Fluorescein (in 0.001 M KOH) and KI	+2	− .97	− .67
Anthracene sulfonic acid and KI	+1	− .81	− .51
Anthracene sulfonic acid and KCNS	+1	− .90	− .60

In order to compare these results with the theoretical equation (3) it would be necessary to know the radii, r, of the critical complexes. Since these are not known a quantitative check is not possible. The values obtained for log k_0/k_0^0 correspond to values of r of the order of 10^{-7} cm. if the rest of the equation is assumed accurate. One fact which appears to be contradictory to the equation is that the corrected values of log k_0/k_0^0 are essentially the same whether $Z_A Z_B$ is one or two. This may be only an apparent discrepancy since the radii of the critical complexes may easily vary as much as a factor of two. It is to be noted that the sign of the effect is always right.

Conclusions.—The simultaneous alteration of more than one variable, as has been necessary in some of our experiments, puts a practical limit on the quantitative comparison of the data with the theoretical equations. It is possible to draw some definite conclusions from our data. In the first place little or no activation energy is required for the quenching process. If it is assumed that the number of collisions in the least viscous solvent can be calculated by gas kinetic theory, then our quenching constants correspond to deactivation in one out of every ten to a hundred collisions.

The significance of the term "collision" is rather uncertain in these solutions especially when it is considered that the participants must stay together a time comparable with the relaxation time of the solution if an ionic strength effect is to be found.[9] Any such calculation of effective collision number merely serves as a check on the conclusion that there is no appreciable activation energy required for the process.

The viscosity effect and the effect of a change of dielectric constant on both k and k_0 are in agreement with the theoretical equation as to direction and agree in magnitude as well as can be expected. The fact that the viscosity effect is found in these systems which require no activation energy does not mean that it must be found in all cases. It is perfectly possible that there may be many bimolecular reactions in which the rate of activation of some intermediate complex by the solvent is the rate determining step. In such cases no viscosity effect is to be expected. On the other hand, effects such as we have observed due to the change of dielectric constant must be expected for all bimolecular reactions between ions. There can be no doubt as to the direction of the change of the rate constant but all that can be expected of the numerical magnitude is that it shall fall within the range found in the study of activity coefficients.

Summary

The effects of changes of temperature, viscosity and dielectric constant of the solvent on the quenching of the fluorescence in solution have been studied. The results show that the quenching constant:

1. Decreases as the viscosity increases.

2. Changes with ionic strength in solvents of different dielectric constant as predicted by the equation derived by means of the Debye–Hückel theory and Brönsted's equation for bimolecular reactions.

3. At zero ionic strength, changes as predicted by Scatchard's equation for bimolecular reactions.

4. Increases with temperature but this increase is primarily due to a decrease in the viscosity of the solvent.

(9) This requirement is due to the fact that the ionic atmosphere around an ion is determined by the square of the charge and not just the charge.