[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF CALIFORNIA]

Salt Effects on the Rates of Fast Reactions in Aqueous Solutions

BY WILLIAM E. HARTY AND G. K. ROLLEFSON

RECEIVED APRIL 13, 1954

The effects of inert salts of various ionic types on the quenching of the fluorescence of the doubly positive ion of quinine by bromide ion and of the doubly negative ion of fluorescein by iodide ion have been studied. It is found that the data for the effect of any one salt on a given reaction can be fitted by an equation derived with the aid of the Debye–Hückel theory. However, specific effects must be attributed to each salt in this theoretical treatment. The specific effects are much less in the quenching of fluorescein by iodide if the quenching constant is plotted against the positive ion concentration. It is also found that the quenching constant for the reaction of quinine ion with bromide can be expressed by a function determined by the concentrations and charges of the ions of the added salts but independent of their nature. It is pointed out that plots of this type may be of greater use for the correlation of kinetic data than the usual plots in terms of ionic strength.

It has been a common practice in the discussion of the effects of salts, which do not enter into the net reaction, on the rates of ionic reactions to plot the logarithm of the rate constant against the square root of the ionic strength of the solution. This type of plot is chosen because the Debye–Hückel theory leads to the conclusion that such a plot will be linear and independent of the nature of the added salt at low concentrations of such salts. In most systems data cannot be obtained at sufficiently low concentrations to fit the limiting law and the value of the rate constant at zero ionic strength has to be obtained by a non-linear extrapolation. Recently Olson and Simonson[1] pointed out that with some reactions between ions of like sign a more simple plot is obtained if the rate constant is considered to be a function of the concentration of the ions of opposite sign rather than the ionic strength. It has also been reported by Young and Jones[2] that the Mayer[3] equation for the activity coefficient of an ion leads to the conclusion that at high concentrations the value for a given ion depends much more on the charges and radii of the ions of opposite sign than it does on the properties of ions bearing the same sign. The present investigation was undertaken to test these points of view. The reactions chosen for study were the quenching of the fluorescence of the doubly negative fluorescein ion by iodide ion as an example of a reaction between ions of like sign and the quenching of the fluorescence of the doubly positive ion of quinine as an example of a reaction between ions of opposite sign.

The quantity which we have measured is the quenching constant as defined by the Stern–Volmer equation

$$I_0/I = 1 + k_Q(Q)$$

in which (Q) is the concentration of the added quencher. This constant is the product of the lifetime of the fluorescent substance and the bimolecular rate constant for the quenching process. The lifetime is not affected by the addition of inert salts hence the effects observed on the quenching constant can be assigned to the bimolecular rate constant. In order to compare the absolute values of the rate constants for systems involving different fluorescent substances it is necessary to know the values for the lifetimes. Accurate measurements have been published recently[4] for both quinine and fluorescein so that it has been possible to convert all our observations to such terms.

Reagents Used.—Eastman Kodak Co. fluorescein was dissolved in sodium hydroxide solution, the solution filtered and the fluorescein reprecipitated with acid. This process was repeated three times. The final product was dried to constant weight at 110°. The molar extinction coefficient of a 10^{-5} molar solution of this fluorescein in 0.001 *M* sodium hydroxide was found to be 78.4×10^3 at 4950 Å. The value in the literature is 78.1×10^3.

Potassium hydroxide solution was prepared by dissolving reagent grade compound in hot water until saturated, cooling to precipitate crystals of the hydrate, filtering, dissolving the crystals in water and diluting to a definite volume. The concentration of the solution was determined by titration with dried analytical grade potassium acid phthalate.

Sodium hydroxide solution was prepared by dissolving reagent grade material in water until saturated, filtering the solution and diluting to the desired volume. The concentration was determined by the same method as for the potassium hydroxide.

Merck U.S.P. quinine sulfate was recrystallized three times from water. The final product was dried to constant weight at 110°. Quinine was obtained from some of this product by precipitation from water solution by sodium hydroxide. After washing with hot water until no trace of sulfate could be detected in the filtrate, the quinine was dried to constant weight at 110°. The purified quinine melted at 175–176° as compared to the value in the literature of 175°.

The absorption spectrum of the recrystallized quinine sulfate was identical to that of the quinine dissolved in the same concentration of sulfuric acid and in general agreement with the absorption spectrum given in the International Critical Tables.

Sodium perchlorate solution was prepared by the neutralization of standardized perchloric acid with analytical reagent grade sodium carbonate, boiling off carbon dioxide and diluting to the desired volume.

Lanthanum perchlorate was prepared by permitting lanthanum oxide to react with the required volume of standardized perchloric acid. The residue which failed to dissolve was filtered, washed and ignited. Its weight corresponded to less than a tenth of a per cent. of the original oxide. The lanthanum oxide which was used was prepared by the ignition of C.P. lanthanum oxalate to constant weight at 1200°. A sample of the oxalate was titrated with

---

[1] A. R. Olson and T. R. Simonson, *J. Chem. Phys.*, **17**, 11676 (1949). Since the publication of this paper there has been diversity of opinion as to the origin of the idea. Daniels (*Ann. Rev. Phys. Chem.*, **1**, 250 (1950)) speaks of it as a revolutionary idea. Laidler ("Chemical Kinetics," McGraw-Hill Book Co., New York, N. Y., 1950, p. 127) says that evidently a new theoretical treatment of the behavior (of salt effects) is required. On the other hand Kilpatrick (*Ann. Rev. Phys. Chem.*, **2**, 270 (1951)) says that the idea was proposed in 1922 by Brønsted. There is no doubt about the fact that Brønsted (THIS JOURNAL, **44**, 898 (1922)) said that the activity coefficients of ions depend only on the action of ions of opposite sign and the salting out effect of the solvent. There is also no doubt that after the Debye–Hückel theory came out Brønsted as well as others interested in the effects of inert salts on rates invariably plotted their rate constants as a function of ionic strength. As far as we have been able to discover Olson and Simonson were the first to use the type of plots presented in their paper.

[2] T. F. Young and A. C. Jones, *Ann. Rev. Phys. Chem.*, **3**, 277 (1952).

[3] J. E. Mayer, *J. Chem. Phys.*, **18**, 1426 (1950).

[4] E. A. Bailey, Jr., and G. K. Rollefson, *ibid.*, **21**, 1315 (1953).

standardized permanganate and the available lanthanum oxide calculated. The calculated value agreed within less than 0.2% with the weight found after ignition.

Magnesium perchlorate was prepared by the reaction of reagent grade magnesium oxide, which had been ignited to constant weight at 1200°, with the required volume of standardized perchloric acid.

Sodium pyrophosphate was prepared from C.P. potassium pyrophosphate by precipitation with sodium acetate. The precipitate was recrystallized from water three times and dried to constant weight at 110°. Qualitative tests for potassium ion and phosphate ion in the final product were negative.

The potassium iodide, potassium nitrate, potassium sulfate, potassium citrate, potassium acetate, potassium bromide and sodium sulfate used were reagent grade. They were dried to constant weight and then used without further purification.

Apparatus.—Figure 1 is a schematic diagram of the apparatus used to measure the light intensities. Light from the General Electric AH-4 mercury vapor lamp X was collimated by the lens L, passed through the filter F_1 of No. 5860 Corning glass (this transmits the mercury lines around 3660 Å.), and the beam split by the filter M of No. 7910 Corning glass. One part of the beam passed through the assembly F_2 which consisted of a solution of the fluorescent substance being used in the given set of experiments followed by a Corning 3060 filter which absorbs the ultraviolet light but transmits the fluorescent light from the solution. The other part of the beam passed into the cell C which was set in a water thermostat and contained the fluorescent solution under investigation. The fluorescence from this solution passed through the Corning 3060 filter F_3 to the photocell P_2. The photocells P_1 and P_2 were Weston Photronic Model 594 barrier layer type photocells.

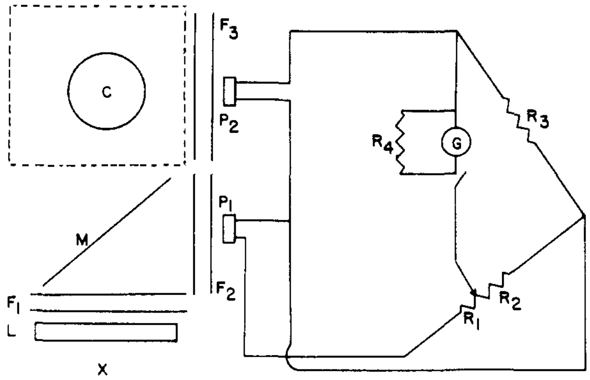

Fig. 1.—Diagram of apparatus.

In any experiment the cell C was one of a set of 2.5 cm. o.d. Pyrex tubes which were made from the same piece of Pyrex stock so that their optical properties would be as nearly alike as possible. The cell, with the fluorescent solution in it, was clamped rigidly in place in the water-bath which was equipped with the devices necessary to control the temperature within a tenth of a degree. The water-bath was a 4.5-liter monel vessel fitted with Corning 7910 windows.

The light intensities were measured by balancing the current from photocell P_2 against that from P_1 by the arrangement shown in the diagram. By this arrangement the intensity of the fluorescent light from C was always determined relative to the intensity of the exciting beam. Hence any effects due to fluctuations in the intensity of the exciting light were cancelled out. Both photocells were cooled with jets of compressed air to eliminate effects due to temperature fluctuations. In order to get the best reproducibility of readings it was found desirable to use peg type resistance for R_1, R_2 and R_3. The galvanometer was a Leeds and Northrup No. 2430 with a resistance of 24 ohms and a sensitivity of 0.003 microamp. per mm. The resistance R_4 was set at the critical damping resistance of 450 ohms. In making the measurements the usual practice was to set the resistance R_3 at 500 ohms and the sum of R_1 and R_2 at 10,000 ohms. Under these conditions, with both cells illuminated and the circuit balanced, the reading of R_2 was proportional to the intensity of the light falling on P_2. Tests were made with screens and filters to check the linearity of this scale. Under typical operating conditions the bridge was easily balanced to 0.1% of the resistance R_2.

The typical experimental procedure was to make consecutive measurements on a set of five sample tubes until at least three sets of readings agreeing to 0.1% or better had been obtained. One of the tubes contained distilled water and served as a measure of the blank due to scattered light which had not been removed by the filters. The other four were divided into two sets of two. One of each set was filled with the fluorescent solution which contained quencher and the other was filled with a solution which was identical with the first except that it contained no quencher. The correction for the distilled water blank amounted to 0.1–0.2% of the intensity of the fluorescence. In order to correct for any differences between tubes the two sets were filled with identical solutions and the intensities measured. This correction ranged from 0.1–0.3%. After making these corrections the values of I_0/I were calculated for each quenched solution. Values for solutions of the same composition but prepared at different times were found to agree within 0.2%. Under the usual experimental conditions the corresponding error in the determination of the quenching constant was about 0.5%.

Experimental Results.—All measurements with quinine were made in 0.01 molal perchloric acid and those with fluorescein in 0.001 molal potassium hydroxide to insure having all of the fluorescer in the form of the divalent ion. In the experiments with fluorescein in which the added salt was sodium pyrophosphate, the hydroxide concentration was raised to 0.005 molal to ensure having the pyrophosphate in the form of the quadrivalent ion. In all experiments the fluorescer was present at a concentration of 10^{-4} M. In the work with quinine the potassium bromide was 0.001 M and in that with fluorescein the potassium iodide was 0.02 M except for one series of experiments in which the iodide was varied from 0.02 to 0.002 M with no inert electrolyte present. Such concentrations gave approximately 25% quenching, which is sufficient to provide good accuracy in the determination of the quenching constants but avoids deviations from the Stern-Volmer law. All measurements were at 25° unless otherwise indicated. The salts added to the quinine–bromide system were all perchlorates. In the fluorescein–iodide system they were always either the potassium or sodium salts. Hence in the tables of data the column headed normality of added salt is always the concentration in moles per liter of the perchlorate ion (or potassium or sodium ion, as the case may be) introduced by the added salt.

The data for the quenching of quinine by bromide are presented in Table I and those for fluorescein by iodide in Tables II and III. (For the sake of brevity, if a reading at a given normality was taken for only one salt it has been omitted from the table, actually some additional readings were obtained for each of the salts.) The ionic strengths of these solutions are 0.01 or higher. This minimum ionic strength is fixed by the fact that in the quinine–bromide reaction the perchloric acid concentration had to be kept at 0.01 M, while in the fluorescein–iodide reaction lowering the

TABLE I

THE QUENCHING OF QUININE ION BY BROMIDE ION IN 0.01 M PERCHLORIC ACID

k, liters/mole			
$NaClO_4$	$Mg(ClO_4)_2$	$La(ClO_4)_3$	Added salt, N
347.0	347.0	347.0	0.0000
306.9	295.5	289.3	.0100
279.7	268.4	260.0	.0200
259.3	249.4	240.7	.0300
247.0	233.1	225.3	.0400
236.0	222.2	214.9	.0500
225.3	212.9	202.8	.0600
212.0	200.4	190.3	.0800
199.9	187.8	179.6	.1000
191.1	179.1	171.6	.1200
181.6	172.1	164.9	.1400
174.8	164.5	158.5	.1600
164.3	152.0	147.0	.2000

potassium iodide concentration below 0.02 *M* reduced the accuracy of the measured values of the quenching constant. Some experiments were run with the latter reaction at lower ionic strength by reducing the iodide concentration and having no other added salt. These results are given in Table IV. Table V shows the effect of temperature on these reactions. The apparent discrepancy between the quenching constants for fluorescein with iodide at 25° as given in this Table and in Table II is caused by a change in the position of the mercury lamp before the data on the temperature effect were taken. The observed quenching constant in this case is somewhat dependent on the geometry.

TABLE II

THE QUENCHING OF FLUORESCEIN ION BY IODIDE ION IN 0.001 *M* POTASSIUM HYDROXIDE

k, liters/mole				Added salt, *N*
KNO_3	$KC_2H_3O_2$	K_2SO_4	$K_3C_6H_5O_7$	
10.04	10.04	10.04	10.04	0.0000
10.80		10.90	10.95	.0100
11.18	11.43	11.33	11.39	.0200
12.11	12.19	12.26	12.30	.0400
12.76	12.96	12.90	12.92	.0600
13.43	13.52	13.67	13.70	.0800
14.17	14.47	14.61	14.58	.1200
14.67	15.16	15.17	15.46	.1600
15.65		16.39	16.55	.2400

TABLE III

THE QUENCHING OF FLUORESCEIN ION BY IODIDE ION IN 0.005 *M* SODIUM HYDROXIDE

k, liters/mole			Added salt, *N*
$NaClO_4$	Na_2SO_4	$Na_4P_2O_7$	
10.34	10.34	10.34	0.0000
11.29	11.57	11.26	.0200
12.25	12.36	12.05	.0400
12.80	12.99	12.66	.0600
13.23	13.55	13.22	.0800
14.03	14.37	14.04	.1200
14.70	15.09	. . .	.1600
15.04	15.52	15.04	.2000

TABLE IV

THE QUENCHING OF FLUORESCEIN ION BY IODIDE ION IN 0.001 *M* POTASSIUM HYDROXIDE

k, liters/mole	Concn. of KI
10.08	0.0200
9.59	.0150
8.94	.0100
8.82	.0080
8.65	.0060
8.25	.0040
7.53	.0020

TABLE V

TEMPERATURE DEPENDENCE OF QUININE–BROMIDE REACTION

Added salt	Added salt, *N*	*k*, liters/mole 25°	35°	45°	55°
. . . . . .	0.0000	347.0	422.0	494.4	575.3
$NaClO_4$	.0200	279.7	338.4	398.3	467.2
	.0800	212.0	253.6	304.1	344.3
	.1600	174.8	214.1	253.9	291.3
$La(ClO_4)_3$	.0100	289.3	354.3	406.5	479.3
	.0400	225.3	276.6	319.2	380.8
	.0800	190.3	227.4	272.8	316.9

TEMPERATURE DEPENDENCE OF FLUORESCEIN–IODIDE REACTION

Added salt	Added salt, *N*	*k*, liters/mole 5°	15°	25°	35°	45°
. . .	0.0000	6.85	8.33	10.20	11.73	12.96
KNO_3	.0200	7.52	9.34	11.42	13.17	14.53
	.0900	9.14	11.13	13.63	15.74	17.65
	.1600	9.95	12.07	14.78	17.23	19.29
	.2400	10.45	12.83	15.87	18.26	20.52
K_2SO_4	.0600	8.58	10.67	13.15	15.01	16.80
	.1082	9.35	11.78	14.39	16.45	18.51
	.1600	10.00	12.51	15.39	17.74	19.75

Discussion

First, we shall compare our results with the equations derivable from the Debye–Hückel theory. It is apparent from an inspection of the data presented that we are dealing with ionic strengths beyond the range of the limiting law form of that theory. The next approximation leads by the usual methods to the following equation for the rate constant in aqueous solutions at 25°[5]

$$\log k = \log k_0 + 1.018 z_A z_B/(B + 1/\mu^{1/2})$$

Strictly speaking, this equation applies only to the bimolecular rate constant, but since it has been found that the lifetime of the fluorescent substance is not dependent on the concentration of the inert salts present we may apply the equation to the experimental values of the quenching constant. Since k_0 is the value at zero ionic strength it should be the same for all solutions involving the same fluorescer and quencher. In testing the equation we have treated k_0 as a possible variable since the derivation of the above equation assumes the theoretical value for the limiting slope and we did not wish to introduce any other fixed values. A graphical test of the equation is obtained by plotting log *k* against the reciprocal of $B + 1/\mu^{1/2}$. A typical plot of this kind is shown in Fig. 2. It is apparent that the data fit the straight line called for by the equation. Similar lines were obtained for the data with the other added salts. In some cases the point at the lowest ionic strength was off the line which may be because of experimental error or may be caused by the fact that *B* is dependent on the nature of the

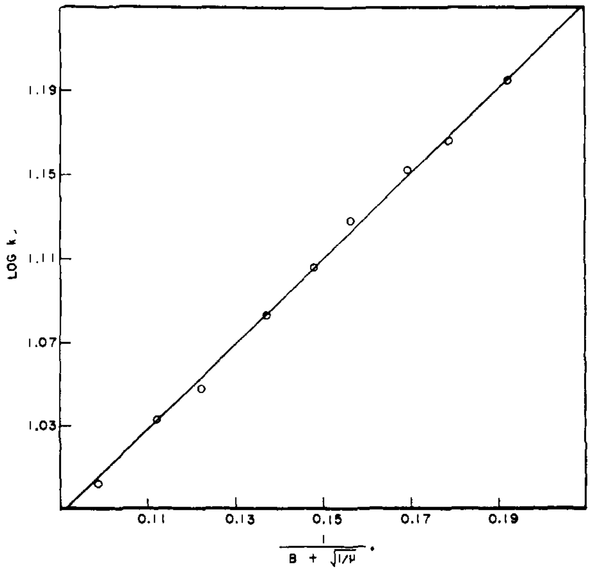

Fig. 2.—Effect of potassium nitrate on the rate of the fluorescein–iodide reaction.

---

[5] *Cf.* A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 138.

salt making up the ionic strength. At high ionic strengths the added salt is the dominating factor in determining the value of B but for low concentrations some deviation may be found because of the fact that under such conditions the fluorescer and quencher are dominant in determining the properties of the solution. Least squares were used to determine the best values of log k_0 and B for each added salt and the values are listed in Table VI. In the case of potassium citrate as the added salt the values given are for the best straight line fitting the data although in that case the data could be fitted better with a curve. Inspection of the Table shows that the variation in log k_0 is negligible, especially when consideration is given to the amount the data have to be extrapolated to fix this value. The values of B can be varied slightly from the ones given but we believed that such a change could not be greater than about 5% without showing a noticeable deviation of the data from the theoretical curve.

TABLE VI

PARAMETERS USED IN TEST OF DEBYE–HÜCKEL THEORY

Added salt	B	log k_0	"a," Å.
KNO_3	3.24	0.804	9.86
$KC_2H_3O_2$	3.00	.800	9.13
K_2SO_4	3.26	.790	9.92
$K_3C_6H_5O_7$	3.43	.785	10.44
KI	2.70	.790	8.22
$NaClO_4$	3.27	.802	9.95
Na_2SO_4	3.38	.793	10.29
$Na_4P_2O_7$	3.64	.769	11.08
$NaClO_4$	1.88	2.717	5.72
$Mg(ClO_4)_2$	2.06	2.721	6.27
$La(ClO_4)_3$	2.12	2.728	6.45

The previous treatment indicates that our data are compatible with the usual method of applying the theory of Debye and Hückel to data of this kind. In order to apply the ideas of Olson and Simonson to our data we have made the plot of k *vs.* concentration of positive ion shown in Fig. 3. It is apparent from the figure that there is little dependence on the nature of the negative ion until rather high concentrations of added salt was reached. If k is plotted against ionic strength instead of the concentration of positive ion for these solutions the curves for the different solutions are distinctly separated although each curve can be fitted as described in the previous paragraph by an equation based on the Debye–Hückel theory. The reaction between quinine and bromide ions cannot be expected to depend on the concentration of ions of one sign since it is a reaction between a doubly positive and a singly negative ion. If the quenching constants in this system are plotted against the concentration of negative ions (with the idea that the effect on the doubly charged positive ion will be dominant) it is found that the curves for the different added salts are closer together than when the data are plotted against ionic strength but there are still marked specific differences.

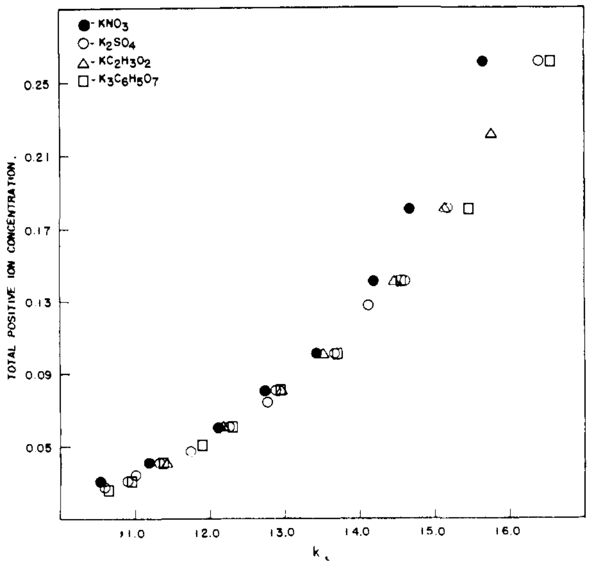

Fig. 3.—Plot of quenching constant for iodide on fluorescein against the positive ion concentration.

In the course of discussion with our colleagues it was suggested by Professor R. E. Connick that the idea emphasized by Olson and Simonson to the effect that ions are influenced primarily by ions of opposite sign may be applied to the quinine–bromide reaction in a simple empirical way. Let us assume that the salt effect is to be calculated in the usual way except that instead of using the ionic strength in calculating the effect on each ion we use only that part of the ionic strength contributed by the ions of opposite sign. Thus for the quinine ion we will consider only the effect of the negative ions and for the bromide ions only the effect of the positive ions. This leads to a limiting law of the form $k = k_0\,10^{-0.509(\mu^{1/2}{}_+ + 3\mu^{1/2}{}_-)}$, or when the limiting law does not apply it suggests that the data should

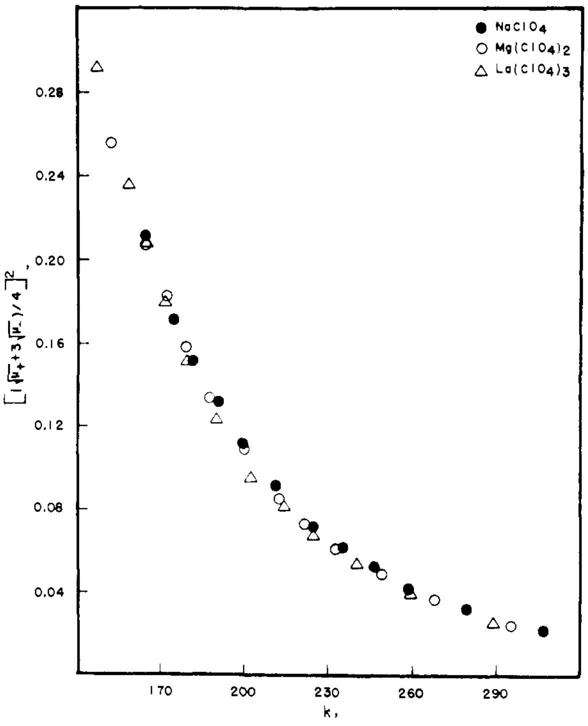

Fig. 4.—The data of Table I plotted against the function $[(\mu_+{}^{1/2} + 3\mu_-{}^{1/2})/4]^2$.

be plotted against $\mu^{1/2}_{+} + 3\mu^{1/2}_{-}$ rather than against the ordinary ionic strength. Such a plot is shown in Fig. 4. It is apparent that the data can be fitted within the limits of experimental error by a single curve. For the present this method of plotting the data must be considered as purely empirical although it was suggested by some theoretical considerations.

The analysis of the effect of temperature on the quenching process is complicated by the fact that the quenching constant is the product of the lifetime of the excited molecule and a bimolecular rate constant. If the lifetime is constant the entire temperature effect is that on the bimolecular rate constant. Then a straight line should be obtained if the logarithm of the quenching constant is plotted against the reciprocal of the absolute temperature. We found that with both the systems studied in this paper such a plot yields a curved line. Such a curvature could be caused by a variation of the lifetime with temperature. Actually, Lewschin[6] has reported that the fluorescence yield from solutions of fluorescein decreases as the temperature is raised. A decreased yield can be caused by the lifetime being decreased by an increase in the rates of the competing first order reactions. It is possible now to measure lifetimes of solutions such as these with sufficient accuracy to test such an explanation; therefore, we shall defer further discussion of the temperature effects until such measurements are available.

The conclusions which may be drawn from the data we have presented are not as definite as we had hoped that they might be. Certainly the fit with the straight line based on the Debye–Hückel theory, which is shown in Fig. 2, must be taken as support for the equation based on that theory, although it does not necessarily confirm the physical interpretation put on the parameters. On the other hand, the curves shown in Fig. 3 and Fig. 4 indicate that specific effects are less pronounced if stress is laid on the effect of ions of opposite sign to those under consideration. On the basis of our experience we would say that rate constants determined in solutions of variable ionic constitution can be correlated best by plots of the type shown in the latter figures.

BERKELEY, CALIFORNIA

---

(6) W. L. Lewschin, *Z. physik*, **43**, 230 (1927).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES, NORTHWESTERN UNIVERSITY]

Structure and Reactivity in the Vapor-Phase Photolysis of Ketones. I. Methyl Cyclopropyl Ketone[1,2]

BY J. N. PITTS, JR., AND I. NORMAN

RECEIVED MARCH 24, 1954

The vapor-phase photolysis of methyl cyclopropyl ketone at 2654–2537 Å. leads primarily to rearrangement giving methyl propenyl ketone with a quantum yield of 0.31 ± 0.02 from 25 to 120°. The probability of dissociation of the parent ketone into radicals must be small, since the quantum yield of carbon monoxide is only 0.12 at 170°. Minor non-condensable products are 1-butene, propylene, ethane, methane, ethylene and biallyl and, for the runs above 100°, traces of cyclopropane. A reaction sequence is proposed that accounts for the olefinic nature of the non-condensable products, and the formation of the α,β-unsaturated ketone.

In recent years it has become increasingly evident that the structures of alkyl substituents have a pronounced effect upon the primary modes of photodecomposition of simple aliphatic ketones.[3] It is now recognized that all simple aliphatic ketones photodissociate to some extent by a Norrish Type I free radical process[4] to give alkyl and acyl radicals. Acetone,[3b,5] methyl ethyl ketone,[6–8] and diethyl ketone[9] decompose almost exclusively in this manner. However, ketones with larger alkyl groups, such as methyl *n*-propyl ketone,[3b] di-*n*-propyl ketone,[10] and methyl *n*-butyl ketone,[11] also react to a significant extent by an intramolecular rearrangement that gives a lower ketone and an olefin. The relative probabilities of dissociation of the bonds adjacent to the carbonyl chromophore also seem to depend upon the nature of the substituents. For example, in the photolysis of methyl ethyl ketone at 3130 Å. the primary split into ethyl and acetyl radicals is highly favored over the competing process that yields methyl and propionyl radicals.[6,8,12]

In view of these results it seemed worthwhile to initiate a study of the vapor-phase photolysis of several types of relatively simple ketones having cycloalkyl or alkenyl substituents. An attempt is now being made to evaluate the influence of these types of substituents on primary processes, and to study the secondary reactions of the radicals produced therein. This paper presents the results obtained from a study of the photolysis of methyl cyclopropyl ketone at 2654–2537 Å. and temperatures from 25 to 170°.

---

(1) Presented at the Los Angeles Meeting of the American Chemical Society, March, 1953.

(2) Taken from the doctoral dissertation of I. Norman, Northwestern University, 1953.

(3) See the comprehensive reviews, (a) W. Davis, Jr., *Chem. Revs.*, **40**, 201 (1947); (b) A. J. C. Nicholson, *Rev. Pure and Applied Chem.*, **2**, 174 (1952).

(4) R. G. W. Norrish and M. E. S. Appleyard, *J. Chem. Soc.*, 874 (1934).

(5) W. A. Noyes, Jr., and L. M. Dorfman, *J. Chem. Phys.*, **16**, 788 (1948).

(6) V. R. Ells and W. A. Noyes, Jr., THIS JOURNAL, **61**, 2492 (1939).

(7) W. J. Moore and H. S. Taylor, *J. Chem. Phys.*, **8**, 466 (1940).

(8) J. N. Pitts, Jr., and F. E. Blacet, THIS JOURNAL, **72**, 2810 (1950).

(9) K. O. Kutschke, M. J. H. Wijnen and E. W. R. Steacie, *ibid.*, **74**, 714 (1952).

(10) C. R. Masson, *ibid.*, **74**, 4731 (1952).

(11) W. Davis, Jr., and W. A. Noyes, Jr., *ibid.*, **69**, 2513 (1947).

(12) G. R. Martin and H. C. Sutton, *Trans. Faraday Soc.*, **48**, 823 (1952).