

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

The Kinetics of the Decomposition of Trinitrobenzoates in Ethyl Alcohol

BY FRANK H. VERHOEK

In a previous paper,¹ in which the rate of decomposition of trichloroacetates was studied in several solvents, the hypothesis was made that the rate-determining step was the unimolecular decomposition of the trichloroacetate ion, forming carbon dioxide and the anion of the acid chloroform, CCl_3^- . In support of this hypothesis the behavior of 2,4,6-trinitrobenzoic acid, which also splits off carbon dioxide, was cited. In this case the other product of the reaction, symmetrical trinitrobenzene, is known to be acidic; an ion of the sort $(\text{NO}_2)_3\text{C}_6\text{H}_2^-$ formed by the decomposition

$$(\text{NO}_2)_3\text{C}_6\text{H}_2\text{COO}^- \longrightarrow (\text{NO}_2)_3\text{C}_6\text{H}_2^- + \text{CO}_2 \quad (1)$$

could therefore exist. That the decomposition of trinitrobenzoic acid was exactly analogous to that of trichloroacetic acid, decomposing as the acid anion rather than as the undissociated acid, was indicated by the observation of Moelwyn-Hughes and Hinshelwood² that trinitrobenzoic acid decomposed to trinitrobenzene and carbon dioxide more rapidly in moist solvents than in solvents which had been carefully dried.

The present investigation was undertaken to test the hypothesis that the rate-determining step in the decomposition of trinitrobenzoic acid was the unimolecular decomposition of the trinitrobenzoate ion, and to compare the behavior of this substance with that of the trichloroacetates studied previously. In order to study the change in rate with change in ion concentration, it is necessary to use a more weakly basic solvent than water, in which the ionization of trinitrobenzoic acid is nearly complete, and ethyl alcohol was chosen. Alcohol has a further advantage over water in that the decomposition is much more rapid in it than in water, the reaction proceeding at 35° in alcohol at about the same rate as at 70° in water. This paper reports the results of kinetic studies of the decomposition of the lithium and sodium salts of 2,4,6-trinitrobenzoic acid, and of salts of trinitrobenzoic acid with aniline and substituted anilines, all in anhydrous ethyl alcohol.

Experimental

The experimental method consisted in dissolving appropriate quantities of the constituents of the reaction mix-

(1) Verhoek, *THIS JOURNAL*, **56**, 571 (1934).

(2) Moelwyn-Hughes and Hinshelwood, *Proc. Roy. Soc. (London)*, **A131**, 177 (1931).

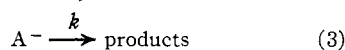
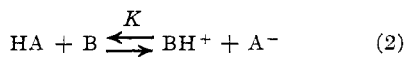
ture in cold ethyl alcohol and pipetting 10-ml. samples into small reaction flasks of about 50-ml. capacity. The flasks were then sealed, placed in thermostats at 35 or 45°, and shaken vigorously for the first few minutes to increase the rapidity with which the solutions came to the temperature of the bath. At suitable intervals a flask was removed from the thermostat, an excess of standard hydrochloric acid added to decompose the alkali-metal ethyl carbonate formed in the case of the inorganic salts, or water added for the reaction mixtures containing anilines, and carbon dioxide-free air bubbled through the solution for fifteen or twenty minutes to remove carbon dioxide. The excess hydrochloric acid or the anilinium trinitrobenzoate remaining was then titrated potentiometrically with standard sodium hydroxide in a carbon dioxide-free atmosphere, using antimony and calomel electrodes. Potentiometric titration was necessary because, especially in the case of the alkaline solutions from the decomposition of the inorganic salts, a deep red color forms which is not immediately removed on the addition of acid, obscuring any possible color change in an indicator. The reaction flasks were chosen large enough so that the titrations could be carried out directly in them, preventing loss which might otherwise occur on transferring from a reaction tube to a titration vessel. The initial concentration was obtained for each experiment in the case of the inorganic salts by the titration of two samples which had been allowed to react to completion; in the case of the mixtures containing anilines by direct titration of two samples before the reaction had begun.

Lithium and sodium trinitrobenzoates were prepared by neutralizing solutions of trinitrobenzoic acid in 95% alcohol with lithium carbonate or sodium hydroxide, recrystallized by dissolving in glacial acetic acid and precipitating with ether, washed with ether until free from acid, and allowed to stand in a vacuum over soda lime. The anilinium salts were prepared by mixing ether solutions of equivalent quantities of trinitrobenzoic acid and the aniline in question, washing the precipitate with ether containing a little trinitrobenzoic acid, then with ether, and drying in a vacuum. Anilinium trinitrobenzoate itself, with which most of the experiments were made, was reprecipitated from acetic acid solution with ether, as in the preparation of the inorganic salts. Dimethylanilinium trinitrobenzoate becomes salmon pink in color on standing for a few weeks, and *p*-toluidinium trinitrobenzoate turns dark yellow on exposure to daylight for several months.

The solvent was prepared by refluxing 95% ethyl alcohol over lime and distilling from lime.

Anilinium Salts.—If the decomposing substance is the trinitrobenzoate ion, the concentration of that ion and hence the rate of decomposition may be changed by adding varying amounts of a weak base such as aniline to a solution containing trinitrobenzoic acid. The behavior of

the reaction is then determined by the equilibrium (2) and the decomposition (3)



In the absence of added anilinium ion, the concentration of the anion A^- may be expressed in terms of the concentrations of acid HA and base B as in equation (4), so that

$$-d[\text{HA}]/dt = k[\text{A}^-] = k\sqrt{K}\sqrt{[\text{B}]}\sqrt{[\text{HA}]} \quad (4)$$

The equilibrium constant K can in turn be expressed in terms of the dissociation constants of the acid K_{HA} and of the cation K_{BH^+}

$$-\frac{d[\text{HA}]}{dt} = k\sqrt{\frac{K_{\text{HA}}}{K_{\text{BH}^+}}}\sqrt{[\text{B}]}\sqrt{[\text{HA}]} \quad (5)$$

If the ionization is not too great, or in any case as a first approximation, the values of $[\text{B}]$ and $[\text{HA}]$ substituted in (5) may be the measured stoichiometric values, as if no acid nor base had disappeared by the formation of ions. Several experimental tests of this equation have been carried out.

The equation predicts that the reaction velocity should be of the one-half order with respect to the concentration of trinitrobenzoic acid, HA. Integration for a given experiment, for which the concentration of base is a constant, b , since no base is used in the reaction, gives

$$\sqrt{[\text{HA}]} = -k'\sqrt{b}t + \text{constant} \quad (6)$$

where
$$k' = \frac{k}{2}\sqrt{\frac{K_{\text{HA}}}{K_{\text{BH}^+}}}$$

Equation (6) shows that a plot of the square root of the concentration of trinitrobenzoic acid given by the titration data against the time should give a straight line of slope $-k'\sqrt{b}$. Such a plot for the decomposition at 35° for a solution made up 0.00503 m in anilinium trinitrobenzoate and 0.00499 m in excess trinitrobenzoic acid is shown in Fig. 1. The slope of the curve divided by $\sqrt{0.00503}$ gives the value $k' = 1.77 \times 10^{-5}$ sec.⁻¹. Good straight lines showing the one-half order course of the reaction are obtained as long as the concentration of base is not more than twice as great as the concentration of acid; at higher ratios of base to acid the order of reaction becomes greater, approaching first order with a very large excess of base over acid. This is to be expected, since with high ratios of base to acid the equilibrium (2) will be shifted far toward the right, and the approximation that the concentration of an-

ion may be expressed in terms of the stoichiometric concentrations of HA and B will no longer be a good one.

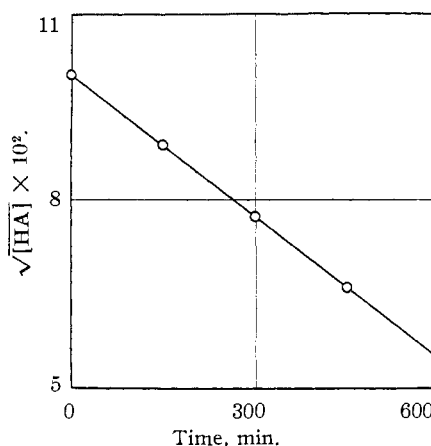


Fig. 1.—Decomposition at 35° when $a = 0.01002 m$, $b = 0.00503 m$.

Equation (5) also requires that the reaction velocity should increase as the square root of the base concentration, b , at constant initial acid concentration, a . Data to test this for the base aniline at initial concentrations of trinitrobenzoic acid near 0.01 m are shown in Table I, from which the values at 35° are plotted in Fig. 2. Since the order of reaction changes as the excess of aniline over acid increases, the values recorded are initial rates, so that the data may be compared over the whole range of aniline concentration. Equation (5) is seen to be obeyed for ratios of base to acid not greater than two to one. One-half the slope of the curve in Fig. 2 gives a value of k' equal to 1.74×10^{-5} sec.⁻¹, in agreement with the value found for the single experiment in Fig. 1, and the values in Table II. A plot of the data at 45° in Table I is exactly similar to Fig. 2, and gives a value of k' at 45° equal to 6.78×10^{-5} sec.⁻¹.

TABLE I
EFFECT OF CHANGING ANILINE CONCENTRATION

Concn. of acid (m./l. $\times 10^3$)	Concn. of aniline (m./l. $\times 10^3$)	Initial rates (m./l./sec. $\times 10^7$)		$\sqrt{a \times b}$ (m./l. $\times 10^3$)
		35°	45°	
9.94	1.969	1.23	4.49	4.425
9.91	4.877		9.48	6.950
10.01	5.025	2.46	9.67	7.093
10.05	10.05	3.52	13.13	10.05
10.03	14.50	4.19	16.60	12.06
10.06	20.03	4.63	18.80	14.19
9.99	40.92	5.20	22.79	20.23
9.93	79.50	5.77	24.26	28.09
9.94	99.3	5.72	24.53	31.43
10.01	106.4	5.98	25.04	32.64

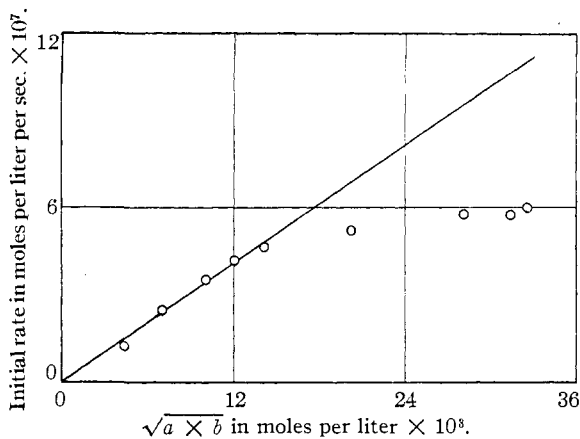


Fig. 2.—Change of initial rate with aniline concentration at 35°.

The behavior of the reaction at constant ratios of acid to base, but at different total concentrations, has been examined. Values of k' for varying concentrations of the salt anilinium trinitrobenzoate obtained from graphs like that in Fig. 1 are shown in Table II. The average values are in good agreement with those obtained from Fig. 2.

TABLE II

EFFECT OF CHANGE IN INITIAL CONCENTRATION ON THE VELOCITY CONSTANT FOR ANILINIUM TRINITROBENZOATE

Initial concn. (m./l. $\times 10^3$)	$k' \times 10^6$	
	35°	45°
4.85	1.736	6.81
8.76	1.744	6.83
10.05	1.728	6.52
19.94	1.816	7.00

A further test of equation (5) may be obtained by investigating the change in velocity with changing strength of base. If values of k' in equation (6) are determined for several different bases, it is evident that a plot of $\log k'$ against $\log(1/K_{BH^+}) = pK_{BH^+}$ should give a straight line of slope 0.5. Values of k' for several substituted anilines, obtained from experiments with equivalent quantities of base and trinitrobenzoic acid at concentrations close to 0.01 m , are given in Table III and plotted in Fig. 3. Since the dissociation

TABLE III

CHANGE OF RATE OF DECOMPOSITION WITH CHANGE IN STRENGTH OF BASE

Base	pK_{BH^+} in water	$-\log k'$	
		35°	45°
<i>o</i> -Chloroaniline	2.68	5.773	5.182
<i>m</i> -Chloroaniline	3.54	5.313	4.738
<i>p</i> -Chloroaniline	4.03	5.116	4.544
Aniline	4.69	4.762	4.186
<i>p</i> -Toluidine	5.17	4.633	4.034
Dimethylaniline	5.21	5.211	4.638

constants in alcohol are not known for all of the cation acids, the values of pK in water tabulated by Brönsted, Delbanco and Tovberg-Jensen³ have been used. The curves in Fig. 3 have been drawn through the point for anilinium trinitrobenzoate with a slope of one-half; it is evident that equation (5) is obeyed satisfactorily for primary bases. At the same time the figure shows that the relative strength of these bases in alcohol is the same as in water. The value of k' for dimethylanilinium trinitrobenzoate, however, is much smaller than would be expected from equation (5). A part of this discrepancy may be due to the fact that the pK values used are those in water, and that the change in strength for dimethylanilinium ion in passing from water to alcohol may be different from that for the primary ammonium ions. However, the data of Deyrup indicate that the ratio of the strength of anilinium ion to dimethylanilinium ion is nearly the same in alcohol as in water.⁴

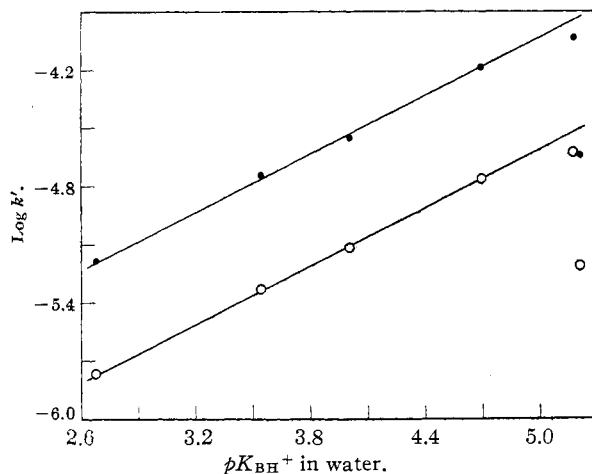


Fig. 3.—Change in rate with change in strength of base: circles, 35°; dots, 45°.

A similar difference in the effect of primary and tertiary amines has been reported for the decomposition of acetoacetic acid,⁵ but the explanation for this case offered by Pedersen,⁶ which requires the presence of a keto group, cannot apply to the trinitrobenzoates.

One would predict that the equilibrium (2)

(3) Brönsted, Delbanco and Tovberg-Jensen, *Z. physik. Chem.*, **169**, 373 (1934).

(4) Deyrup, *THIS JOURNAL*, **56**, 60 (1934). The older data of Goldschmidt [*Z. physik. Chem.*, **99**, 116 (1916)], on the other hand, show dimethylanilinium ion to be stronger than anilinium ion in alcohol by 1.3 pK units, which would move the dimethylanilinium point horizontally somewhat to the left of the curve shown in Fig. 3.

(5) Widmark, *Acta Med. Scand.*, **53**, 393 (1920); *Skand. Arch. Physiol.*, **42**, 43 (1922); Ljunggren, Dissertation, Lund, 1925.

(6) K. J. Pedersen, *J. Phys. Chem.*, **38**, 570 (1934).

would shift to the right on the addition of a neutral salt to the reaction mixture as a result of a salt effect on the constant K , with a consequent increase in the reaction velocity. A slight effect of this sort was observed in an experiment in which lithium chloride to the concentration $0.102\ m$ was added to anilinium trinitrobenzoate at a concentration $0.0100\ m$. The initial rates were 14.0×10^{-7} mole per liter per second and 3.97×10^{-7} mole per liter per second at 45 and 35° , respectively, as compared with the values 13.1×10^{-7} and 3.52×10^{-7} in the absence of lithium chloride.

The equilibrium (2) should be shifted to the left by the addition of anilinium ion, decreasing the concentration of trinitrobenzoate ion and the reaction velocity. This effect was shown in an experiment in which anilinium benzenesulfonate to a concentration $0.01005\ m$ was added to a solution $0.00993\ m$ in anilinium trinitrobenzoate. The initial rates at 45 and 35° were 9.72×10^{-7} and 2.85×10^{-7} mole per liter per second, respectively. These values are again to be compared with those for a solution containing anilinium trinitrobenzoate alone: 13.1×10^{-7} and 3.52×10^{-7} .

Inorganic Salts.—The decompositions of lithium and sodium trinitrobenzoates in ethyl alcohol approximate closely to first-order reactions. This is the predicted behavior if the salts are completely dissociated and the decomposing substance is the trinitrobenzoate ion. A plot of the logarithm of the trinitrobenzoate concentration against the time for sodium trinitrobenzoate at 45° is shown in Fig. 4. The deviation of the points for the latter portion of the reaction from the straight line curve is typical, although it is often not as noticeable even as in Fig. 4. This deviation is probably the result of a side or consecutive reaction which causes removal of alkali. The solutions turn deep red as they become more strongly basic, and the alkali thus used is not immediately available for neutralizing acid, as shown by the fact that the solutions are not decolorized when acid is added. In consequence more sodium hydroxide is required to titrate the excess hydrochloric acid added to neutralize the bicarbonate formed by the decomposition, and more trinitrobenzoate appears to be left undecomposed at a given time, than is actually the case. The effect is to cause the points on a first-order plot to lie above the straight line toward the end of the

reaction, as Fig. 4 shows. This effect is more marked the higher the concentration.

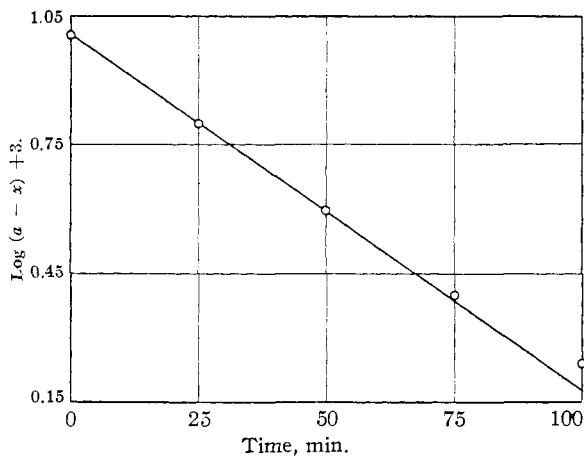


Fig. 4.—The decomposition of sodium trinitrobenzoate at 45° .

Table IV summarizes the results for the decomposition of lithium and sodium trinitrobenzoates at 35 and 45° . In view of the deviation of

Salt	Concn. (m./l. $\times 10^3$)	k (sec. $^{-1} \times 10^3$)	
		35°	45°
Li	4.82	7.69	31.1
Li	9.96	7.00	28.4
Na	10.02	6.99	29.4
Li	10.18	7.40	29.9
Li	19.88	6.18	24.3
Li + $0.174\ m$ LiCl	10.18	4.29	17.1

the experimental points from those for a first-order reaction, the data have been recorded as first-order velocity constants calculated from the initial concentrations and initial rates obtained by drawing tangents to concentration-time curves at zero time. The values of these constants do not differ appreciably from those obtained from first-order plots as in Fig. 4. The table shows that the velocity constants at different concentrations satisfy the assumption of a first-order reaction, but that there is some trend toward more rapid reaction at lower concentrations.

The addition of lithium chloride to the reaction mixture causes the reaction to proceed more slowly, as shown in the last line of Table IV. The decrease in rate observed, however, is not as great as would be predicted on the simple assumption that the addition of lithium ion caused the ionization of lithium trinitrobenzoate to be suppressed, with a decrease in the trinitrobenzoate

ion concentration and a consequent decrease in the reaction rate.

Discussion

The data reported above indicate beyond reasonable doubt that the decomposing substance in the decomposition of trinitrobenzoates in ethyl alcohol is the trinitrobenzoate ion. It would be desirable if the data on the decomposition of the anilinium salts could be treated in such a way as to allow a determination of the equilibrium constant K . If the inorganic salts are assumed to be completely dissociated, the ratio of the initial rates recorded in Table I to the average value of the initial rates for the inorganic salts at 0.01 m , multiplied by the values of a in Table I, give the concentrations of trinitrobenzoate ion in each of the reaction mixtures in the table. From the

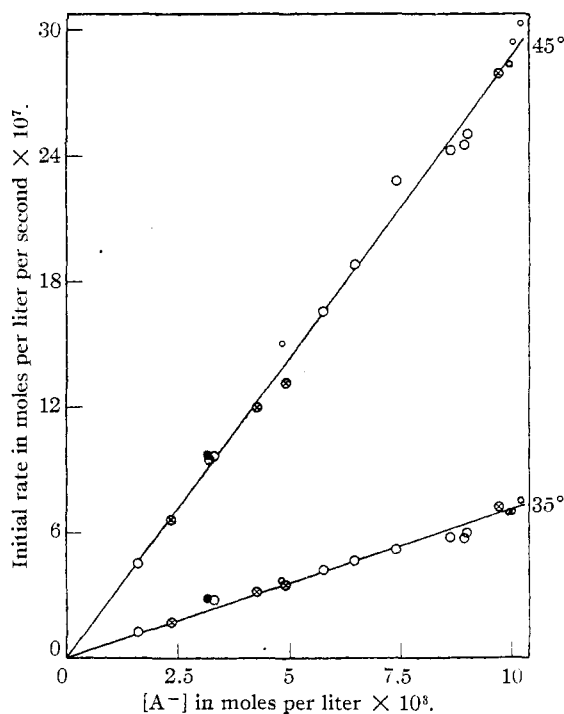


Fig. 5.—Change in rate with trinitrobenzoate ion concentration.

values of ion concentrations calculated from the rates at 35° and the initial concentrations of trinitrobenzoic acid and aniline, values of K for the aniline-trinitrobenzoic acid equilibrium ranging from 0.4 to 1.4 are found. If the value of K is that large, it is not surprising that it is only when the ratio of acid to base is not too far from unity that the reaction is found to be of the one-half order and that the initial rates vary with the

square root of the product of the initial concentrations of acid and base, for about one-half of the acid and base disappears to form ions by the equilibrium (2). The concentrations of acid and base to be introduced into equations (4) or (5) are then much less than the amounts initially added.

The reasonableness of the values of K quoted above has been tested by choosing the value 0.9 for the equilibrium constant for the reaction between aniline and trinitrobenzoic acid, calculating the initial concentration of trinitrobenzoate ion for each reaction mixture, and plotting the initial rate of reaction against the ion concentration. Such a plot is shown in Fig. 5; the large open circles indicate points for ratios of acid to base different from unity (Table I), the crossed circles points for which $a = b$ (Table II), the small circles points for the inorganic salts (Table IV), and the solid circles points with added anilinium ion. The distribution of the points about a straight line at each temperature, showing the direct dependence of the reaction velocity on the concentration of trinitrobenzoate ion, is entirely satisfactory.

If the equilibrium constant for the trinitrobenzoic acid-aniline reaction in alcohol is taken as 0.9, and the dissociation constant for anilinium ion in alcohol has the value 1.9×10^{-4} given for 25° by Deyrup,⁴ then the dissociation constant of trinitrobenzoic acid in alcohol is 1.7×10^{-4} . From conductivity measurements Braun⁷ obtained the value 2×10^{-6} .

The slopes of the curves in Fig. 5 give the velocity constants for the unimolecular decomposition of the trinitrobenzoate ion; the values are $7.18 \times 10^{-5} \text{ sec.}^{-1}$ and $28.7 \times 10^{-5} \text{ sec.}^{-1}$ at 35 and 45°, respectively. From these one calculates the energy of activation to be 27,000 calories per mole. This value is lower than the value 29,970 found by Moelwyn-Hughes and Hinshelwood² for the decomposition of the free acid in water. If it is safe to assume that trinitrobenzoic acid is completely dissociated at the concentrations used by Moelwyn-Hughes and Hinshelwood, this difference in energy of activation may be looked upon as corroborative evidence for the stabilizing effect of solvation on the ion, as suggested for the trichloroacetate decomposition.¹ The ion is considered to be more stable in water because it is more highly solvated in that solvent than in alcohol; decomposition when it does occur involves

(7) Braun, *Z. physik. Chem.*, **85**, 170 (1913).

a greater energy of desolvation, which appears in the higher energy of activation for the decomposition in water.

Summary

1. The decomposition of lithium and sodium trinitrobenzoates in ethyl alcohol has been found to be of the first order.

2. The decomposition of trinitrobenzoic acid in alcohol in the presence of aniline and substituted anilines has been found to be of the one-half order with respect to both acid and base when the ratio of acid to base is not too different from unity. This is the behavior to be expected if the decomposing substance is the trinitrobenzoate ion.

3. Choosing a suitable value for the equilibrium constant of the reaction between aniline and trinitrobenzoic acid, the initial rate of decomposition has been shown to vary directly with the calculated equilibrium concentration of trinitrobenzoate ion.

4. The variation of the rate of decomposition with the strength of the bases added to solutions of trinitrobenzoic acid in alcohol is in agreement with the predicted effect of the change in basic strength on the concentration of trinitrobenzoate ion.

5. The dissociation constant of trinitrobenzoic acid in alcohol has been estimated to be 1.7×10^{-4} .

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE INSTITUTE OF TECHNOLOGY OF THE UNIVERSITY OF MINNESOTA]

Studies on Aging of Precipitates. XXIV. The Apparent Effect of Filtration upon the Aging of Fresh Lead Sulfate. Aging of Lead Sulfate in Excess of Lead and of Sulfate

BY I. M. KOLTHOFF AND WILLIAM VON FISCHER¹

In the present study the speed of aging of freshly precipitated lead sulfate was investigated in solutions containing an excess of lead nitrate or of potassium sulfate. In previous work² it has been found that the speed of penetration of thorium B into lead sulfate under standardized conditions is a good indicator of the progress of the aging of the precipitate and the method was applied to the present work. The samples of lead sulfate after aging were, as a rule, collected by filtration or centrifuging before they were shaken with the radioactive lead solution. The results obtained were very erratic and difficult to explain. It seemed that the method of collecting the precipitate had a great effect upon the speed of penetration of the thorium B. For this reason, the apparent effect of filtration upon the age of the lead sulfate was investigated in the first part of this study.

Apparent Effect of Filtration.—Lead sulfate was prepared by adding to a measured volume of

0.0665 *M* lead nitrate an equal volume of 0.0665 *M* potassium sulfate from a pipet in about twenty seconds (direct precipitation). In a few instances the precipitation was made in the reverse order (reverse precipitation). A precipitate in contact with the above supernatant liquid is called for convenience an "equivalent body." Most of the aging experiments in an excess of lead were made in what we call a "standard lead" solution. This was obtained by adding a lead nitrate solution to the suspension; the final solution was 1.59×10^{-3} *M* in lead nitrate and 0.0652 *M* in potassium nitrate. The experiments with thorium B were carried out in a solution of the same composition. Therefore, if the aging had taken place in the standard lead solution or as an equivalent body, a radioactive lead solution of suitable composition could be added to the suspension after aging without separating the precipitate from the mother liquor. After aging in excess of sulfate or in larger excesses of lead it was necessary to collect the precipitate; the latter was then suspended in a radioactive lead solution prepared by dissolving pure lead nitrate (c. p., thrice recrystallized) and c. p. potassium nitrate in conductivity water and then saturating with lead sulfate. This "syn-

(1) From the experimental work of a thesis submitted by William von Fischer to the Graduate School of the University of Minnesota in partial fulfillment of the requirements of Doctor of Philosophy, December, 1937.

(2) I. M. Kolthoff and Ch. Rosenblum, *THIS JOURNAL*, **56**, (a) 1264, (b) 1658 (1934); **57**, (c) 597, (d) 607, (e) 2573, (f) 2577 (1935); **58**, (g) 116, (h) 121 (1936).