

tralization process. Sometimes this secondary behavior is predictable from familiar considerations based on solvation or tautomerism. However, there are other cases where such considerations do not at present suffice for an adequate explanation.

In an attempt to find new secondary acids and bases, involving in their neutralization small heats of activation, the neutralization process has been studied in numerous cases at temperatures as low as -160°C . (113°K). No new cases of secondary behavior were found. These results indicate a striking distinction between primary and secondary. It is suggested that every secondary acid or base also exists in an independent primary form and that the relative amounts and the difference in energy of the two forms can be ascertained by kinetic studies.

In order to interpret the distinction between the two forms various hypotheses are considered.

The hypothesis that at present seems most probable is that two electromeric forms may exist, incapable of resonance with one another, and differing in the laws which govern electronic distribution. Such a hypothetical electromerism is illustrated not only for acids and bases but also for a certain class of odd molecules.

Our second kinetic thesis concerns systems in which there is resonance between a number of contributing structures. It asserts that a resonating molecule may without activation take part in a reaction characteristic of one of its contributing structures, even though the contribution of that structure may be extremely small and the calculated energy of that structure extremely high. This thesis is demonstrated by experiments upon numerous acids and bases at a very low temperature.

BERKELEY, CALIF.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

Trinitrotriphenylmethide Ion as a Secondary and Primary Base

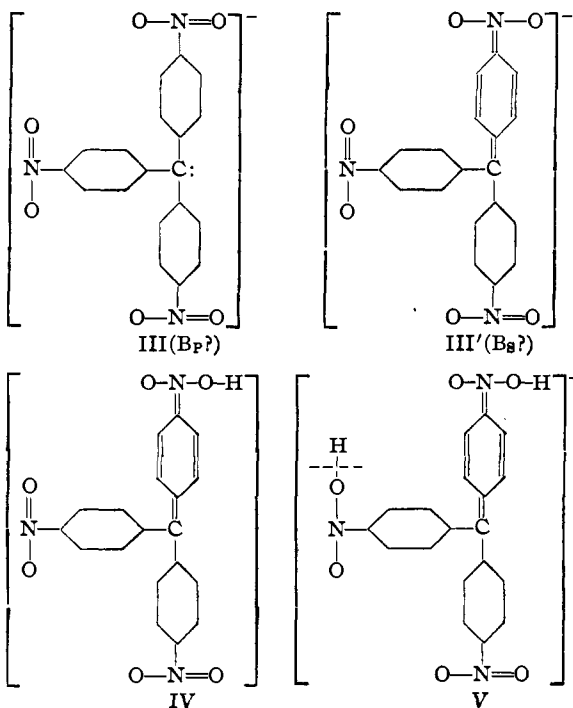
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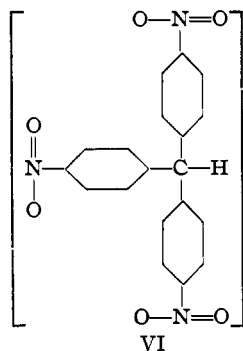
When we started this investigation we were unacquainted with any typical secondary base. It seemed not unlikely, however, by analogy to the variously substituted positive triphenylmethylium ions, all of which behave as secondary acids, that the negative triphenylmethide ions would prove to be secondary bases.

The substance chosen for investigation was 4,4',4''-trinitrotriphenylmethane, which is represented by formula VI in the accompanying graphical scheme. This substance in alkaline alcoholic solution loses hydrogen ion, giving the intensely blue trinitrotriphenylmethide ion which may be represented by formula III'. According to our expectation this solution, when acidified with acetic acid at temperatures ranging from -30 to -80° , fades slowly, and fades more slowly the lower the temperature, thus showing that the blue ion is not behaving as a primary base with respect to the addition of an acid at the central carbon atom.

According to the views expressed in the paper just preceding, a secondary base of this sort should exist in two forms. One form is to be identified with the substance as it ordinarily is, in the

state of a secondary base. The other form, of higher energy, is one in which the substance be-





haves as a primary base. If there are these two forms we must see whether the difference in energy between them can be ascertained from a study of the kinetics of the neutralization process.

We have also discussed certain hypotheses to account for the behavior of secondary acids and bases. It is unnecessary in the present paper to commit ourselves to any hypothesis, but for the sake of clarity we show in formulas III and III' the two states of the trinitrotriphenylmethide ion in terms of the electromeric hypothesis. The former is capable of adding acid directly to the central carbon atom, the latter is not. Since, however, we are now concerned only with our more fundamental assumptions, we shall represent the primary substance as B_P^- and the secondary as B_S^- .

At first we had intended to study the trinitrotriphenylmethide ion only far enough to demonstrate its behavior as a secondary base, but some intricacies of behavior, which were puzzling at first, led us to make an extensive, although not very exact, experimental survey of the kinetics of this system.

When the blue ion has been formed and the central carbon has lost its power of acting immediately as a base, the basic character has, in a certain sense, been transferred to the three nitro groups. Therefore a sufficiently strong acid should attach itself at one of the nitro groups and in this process the blue ion should act as a primary base. This expectation was verified. If to the blue alcoholic solution at low temperature we add hydrochloric acid instead of acetic, a brilliant orange appears. An excess of sodium ethylate restores the blue color and we may titrate back and forth between blue and orange with sodium ethylate and hydrochloric acid. These changes even at -85° are instantaneous. At first it was thought that the orange compound might correspond to formula IV, although it is hard to see

why a compound of that formula should show any color, except perhaps a pale yellow. In fact we shall see that more than one equivalent of H^+ is used in the formation of the orange compound from the blue ion.

The Kinetics of the Neutralization of the Blue Ion.—Trinitrotriphenylmethane, which was kindly prepared for us by Mr. R. L. Caswell, under the direction of Professor T. D. Stewart, may be purified rapidly by successive recrystallizations from toluene and may be kept for weeks unchanged, either as solid or in the toluene solution. In alcohol, especially in the presence of alkali, the substance is sensitive to oxygen and to small amounts of substances of the type of the organic peroxides. A stock solution in toluene was kept and added to alcohol just before each experiment. Our solvent, therefore, in all the experiments to be described, contained by volume 85% absolute ethyl alcohol and 15% toluene, except when otherwise stated. That very nearly the same results would have been obtained in pure alcohol was shown by experiments in which the percentage of toluene was varied.

The reaction vessel in the form of an inverted Y was exhausted to the point where the small amount of residual oxygen no longer had any deleterious effects. This vessel, with the alkaline solution in one limb and the acid in the other, was placed in the low temperature bath (of acetone and carbon dioxide). When the temperature equilibrium was attained the vessel was tipped rapidly back and forth until the contents were thoroughly mixed. The reaction was then followed by comparing the color with a set of standard color tubes. After the experiments had indicated that the reaction was always of first order with respect to the colored ion, the procedure was simplified further. The time was taken merely between the mixing and the matching of a single color standard.

In each experiment one limb of the reaction vessel contained 5.5 cc. of the blue alkaline solution and the other limb contained 1.0 cc. of the acid solution. The concentrations given refer to the total volume of 6.5 cc. after mixing. The initial alkaline solution was always the same and contained 0.0015 *M* sodium ethylate and 0.001 *M* trinitrotriphenylmethane. Later experiments showed that in this solution only one-eighth of the methane is in the form of the blue methide ion. After mixing the reaction was allowed to continue until this ion fell to one-sixteenth of its initial concentration, or a little less than 0.00001 *M*, when the elapsed time was read. The acids varied in concentration from 0.003 to 1.0 *M*, from which we obtain the actual concentration by subtracting the concentration of the ethylate, ignoring the very small concentration of the blue ion.

An accuracy of 10% in the measurement of the time was all that was sought. In a work of this sort, which is prospecting in a large field, it seems undesirable to spend much time upon the refinement of the technique of measurement, or even upon the purification of the reagents. Of the sixteen acids used in the following experiments several were far from pure, and our conclusions

must be drawn from the results as a whole, and not from those obtained with a single acid. There is, moreover, a more fundamental reason for distrusting the generality of results obtained from a given acid. When we are comparing reactions of a given substance with various other substances and under various conditions, it is important that that given substance should be the same in the several experiments. In our case, however, we are going to conclude that this is not in general true. There is every reason to believe that the blue ion in alcohol is a complex between trinitrotriphenylmethide ion and the solvent. Now when a new solute is added, such as one of the acids used for the titration, it may replace some of the solvent molecules in the complex, thus changing the nature of the reacting substance and its heat of activation. We are going to show that at least three substances, phenol, boric acid, and water appear to form such new complexes.

The first experiments were carried out with acetic acid. Here, as with many other acids, the rate of the reaction was found, within our limits of accuracy, to be proportional to the concentration, when the acid concentration is small. At higher concentrations the rate increased less rapidly than the concentration, the discrepancy amounting to 20% at 0.015 *M*. It seems probable that this effect is due to departures from the ideal solution. In the more dilute solutions the reaction may be regarded as strictly bimolecular.

Added salts were found to have no appreciable influence upon the rate, except in the case of silver salts, which produce insoluble compounds with the blue substance. The rate with acetic acid was also found to be unaffected by sodium acetate, showing that the rate is determined solely by the undissociated acid and not by the small concentration of hydrogen ion which is present. It was fortunate that while doubtless many of our solutions were supersaturated at the temperature of the measurements, there was no precipitation during the course of the measurements except in one or two cases, notably in the case where sodium chloroacetate was formed.

Since the reaction was found to be bimolecular and free from catalysis or neutral salt effect, we may calculate the heat of activation without ambiguity. If $-dc_B/dt$ represents the diminution per second of the concentration of the ion B_S^- , the rate constant k is determined by the equation $-dc_B/dt = kc_Ac_B$ where c_A is the molal con-

centration of the acid. Values of k for acetic acid (0.0046 *M*) were obtained at the four temperatures -53 , -63 , -76 and -82° . Plotting $\log k$ against $1/T$ gave a good straight line, the individual departures corresponding to differences in k of only a few per cent. Here, however, we are only testing the experimental method. No such accuracy is claimed for the results as a whole, nor was it desired, as we have already explained.

We shall attempt to interpret our results in terms of the following mechanism.



We assume that (b) is the rate-determining step. Then the concentration of B_P^- depends upon the concentration of B_S^- , the temperature, and the difference in energy between B_P^- and B_S^- . If the reaction proceeds through this mechanism and not through that of the activated complex, the measured heat of activation should be the same for the several acids and equal to the difference in energy between the primary and secondary forms of the base.

We have collected in Table I the results obtained with various acids. The question marks indicate that only one or two observations were made. The acids are arranged according to the ionization constant, K_{H_2O} , in water at room temperature. The ionization constants in alcohol at low temperature are certainly of a quite different order of magnitude but probably are roughly in the same order. The rate constant k at -60° is given in the third column, concentrations being in moles per liter and time in seconds. With the six strongest acids in this list the reaction proved to be bimolecular and from the temperature co-

TABLE I

Acid	$-\log K_{H_2O}$	k	Heat of activation, kcal.
Chloroacetic (+ $CH_2ClCOOLi$)	2.80	30	10.2
Furoic	3.15	10	8.8
α -Naphthoic	3.70	5.3	8.5
Lactic	3.85	3.2	8.9
Benzoic	4.15	5.1	10.0
Acetic	4.75	3.0	8.6
<i>p</i> -Nitrophenol	7.10	1.0 (?)	
2,4-Dichlorophenol	7.55	0.87 (?)	
Hydrocyanic	9.15	.13	
Boric	9.20	.090	
Catechol	9.50	.27 (?) (0.15 <i>M</i>)	
β -Naphthol	9.60	.12	
Phenol	9.85	.090	

efficient of k we have calculated the heats of activation given in column 4.

We regard the several values of the heat of activation as equal within the limits of experimental error and of uncertainties concerning the constancy of composition of the blue ion, of which more will be said later. The average value is 9.1 kcal. which we may take as the difference in energy between the primary and secondary forms of the base. A still more striking verification of the constancy of the heat of activation will be furnished presently. The study of stronger acids than chloroacetic would have been extremely interesting but was prevented by the formation of the orange compound.

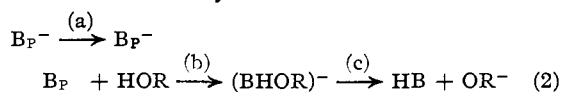
It will be noticed that k increases regularly with acid strength. It appears as though increasing electrical polarization of the acid, by its orienting effect, increases the probability that a given collision between the acid and the primary base will be effective. Taking the highest rate constant, $k = 30$, obtained for chloroacetic acid, we may obtain an idea of the rate constant for the primary base itself. It has become common in a case of this kind to calculate the ratio of the concentrations of two forms from the difference in their energies by means of the Boltzmann equation. Such a calculation shows B_s^- to be 2×10^9 times as concentrated as B_p^- , whence the rate constant for B_p^- would be $30 \times 2 \times 10^9 = 6 \times 10^{10}$. Comparing this with other bimolecular rate constants we would conclude that B_p^- and $CH_2ClCOOH$ have a very large chance of reacting at each collision. We believe, however, that this calculation is erroneous. The ratio of the concentrations depends not only upon the change of energy but also upon the change of entropy. There are no data from which the latter can be calculated but we may make a guess. In going from B_s^- to B_p^- there is likely to be a loss of attached alcohol molecules, together with a loosening of constraints such as those operating upon the nitro groups. Both of these changes would produce an increase in entropy. It is therefore probable that the concentration of B_p^- is considerably larger than that which we have just calculated, and the rate constant correspondingly smaller.

When we come to the weaker acids of Table I the values of k are those calculated formally from the velocity at 0.015 M , but k is no longer a true constant, for the rate is no longer proportional to the acid concentration. The most extreme cases are that of phenol, in which changing from 0.015 to 0.15 M only doubles the rate, and that of boric acid in which, through the same range of concentration, the rate increases by only 10%. This result was at first perplexing. The evidence is entirely against the supposition that either of these two acids is much polymerized in alcohol. Another possible explanation was suggested by

the fact that there are slight but perceptible differences in color when different acids are used. We already have alluded to the possibility that the blue ion in alcohol, which presumably holds alcohol molecules through hydrogen bonds at the three nitro groups, may have some of these alcohol molecules replaced by solute molecules when certain substances are dissolved. The fact that phenol and boric acid give lower rates than hydrocyanic acid and β -naphthol, and also show the least effect of concentration upon reaction rate, suggested that phenol and boric acid displace the alcohol from the nitro groups to an extent depending upon their concentration, and that the ion with phenol attached is less reactive than the corresponding alcohol compound. These assumptions would explain qualitatively both the reduced reaction rate and the small effect of concentration.

In order to test these assumptions quantitatively the rate of fading of the blue color was studied with a mixture containing large amounts of phenol or boric acid and small amounts of acetic or benzoic acid. Although the effects were small, of the order of 10–30%, they were always in the same direction, namely, the rate in the mixture was smaller than that calculated from the behavior of the pure acids. We have, therefore, evidence that boric acid and phenol do form complexes with the reacting substance, which diminish its reactivity, and we shall later obtain more conclusive evidence on this point. On the other hand, the magnitude of the effect is by no means sufficient to account for the fact that the rate with boric acid and phenol is nearly independent of the concentration.

The true explanation of this effect proved to be a very simple one. Alcohol is itself an acid, and although its acid strength is not high enough to cause the fading of the blue color to occur to any great extent before equilibrium is established, it does, in the presence of a stronger acid, play an important and sometimes preponderating part in the mechanism of the fading process. This is due to the relatively large number of alcohol molecules present. Side by side, therefore, with the reaction we have considered so far, is this reaction with the solvent, which may be written as



to which must be added $OR^- + HY \longrightarrow HOR + Y^-$ in the presence of another acid such as phenol.

In order to determine the rate of the pure reaction (2) in the absence of any other acid than alcohol we have proceeded indirectly. In some experiments with *m*-cresol, and also in experiments with phenol to which sodium phenolate was added, the fading of the blue color did not run to an end but came to an equilibrium color. Evidently as concerns its dissociation to form the blue ion, the trinitrotriphenylmethane is an acid of about the same strength as phenol. So also in alcohol containing varying amounts of sodium ethylate we were able to measure the equilibrium ratio of B_S^- to HB. This ratio at a given temperature is proportional to the concentration of ethylate ion and at a given concentration of the latter increases with increasing temperature. From measurements at a series of temperatures, which we shall not give in detail, we were able to obtain the increase in energy in going from $HB + OR^-$ to $HOR + B_S^-$. This amounts to 2.2 kcal. The equilibrium constant $(B_S^-)/(HB)(OR^-)$ at -60° is 15.8.

In certain experiments the color of the equilibrium solution was studied when small amounts of water were added successively to the alcohol. If the ethylate ion is largely hydrolyzed in the presence of small quantities of water, we should expect the essential equilibrium now to be that between $HB + OH^-$ and $H_2O + B_S^-$ and therefore we should expect the amount of color to diminish rapidly as the water is added. In fact no change in color was found until the water had reached nearly 10 mole per cent. At first sight this seemed to indicate that the ethylate ion is not largely hydrolyzed. This, however, is not the probable explanation. We are presently going to produce evidence that water replaces alcohol in the blue ion forming a more stable substance. Apparently this effect is just counteracting the expected effect, when water is added to the solution.

Starting with a solution of trinitrotriphenylmethane in alcohol and adding a solution of sodium ethylate, we were able to study the rate of formation of the blue ion in a range sufficiently remote from equilibrium. The rate of this reaction, which is the reverse of reaction (2), is strictly proportional to the concentration of ethylate ion and of HB. From such measurements at different temperatures we obtained the value of the rate constant at -60° , and the heat of activation, which amounts to 11.1 kcal.

Subtracting from this heat of activation the heat of reaction obtained from the equilibrium measurements, we obtain 8.9 kcal. as the heat of activation of reaction (2). No great accuracy can be claimed for this determination, but the

agreement of this value with the value 9.1 kcal. obtained as a mean for the much stronger acids, ranging from chloroacetic to acetic, very strongly substantiates our assumption that the heat of activation in all these cases is the heat required to form B_P^- from B_S^- . If the activation occurred only at the moment of collision between the reacting molecules, it would be hard to explain why the heat of activation or, in other words, the potential barrier in the activated complex should be the same for such very different substances as alcohol and our other acids.

When we came to determine the rate constant of reaction (2) by finding the ratio between the equilibrium constant and the rate constant in the reverse direction, we expected to find the rate due to the alcohol alone a little smaller than the rate which had been observed with dilute solutions of phenol and boric acid. In fact, however, the rate which we calculated was nearly twice the one observed in the presence of those two substances. This result was at the time so surprising that the whole determination was repeated with greater care, but the result was the same. We see no explanation except in the assumption for which we have already shown other evidence, namely, that the blue ion is a different substance when small amounts of phenol or boric acid are present.

If the blue ion in alcohol itself is not as simple as indicated in structure III', but rather has alcohol molecules attached by hydrogen bonds to the several nitro groups, and if when certain substances such as phenol are added (and this may be true to some extent for any of the other acids we have employed), the solute molecules replace the alcohol molecules in the complex, then these new and more stable molecules may be expected to react more slowly either by reaction (1) or (2). In the course of another investigation we have found that crystal violet in toluene forms complexes with alcohols and acids, and the stability of these compounds reaches a maximum in the case of phenol.

In this connection we may mention the effect of water upon the reaction rates that we have been discussing. If, for example, to a 0.01 molal solution of acetic acid in alcohol we add water to the extent of 2 *M*, the rate of the reaction is reduced by one-half. This effect we attribute mainly to the formation of a stabler complex in which water replaces alcohol in the blue ion.

Colors and Reactions with the Chloroacetic Acids

When to the alkaline solution containing the blue ion B_5^- at low temperatures we add trichloroacetic acid, the same orange color is obtained as with hydrogen chloride and, as in that case, this color fades very slowly compared with the rate of fading of the blue color in the presence of acids like acetic. In other words, trichloroacetic acid, although even at room temperature in alcohol¹ its ionization constant is smaller than that in water by a factor lying between 10^4 and 10^5 , still behaves as a strong acid toward our indicator.

If now we use dichloroacetic acid we obtain the same pure orange color but the fading of this color is much faster. This was interpreted to mean that the solution contains an amount of the blue ion too small to be observed visually, but large enough, because of its much higher specific reaction rate, to permit the rapid disappearance of the orange color. In other words, on account of the rapid equilibrium between orange and blue, the color disappears chiefly through the reaction of the latter. This view was supported by further experiments and it was found possible to make a rough estimate of the fraction of the substance in the blue form.

We wished to ascertain whether the orange substance is produced from the blue by the addition of undissociated acid or by the addition of free hydrogen ion, and by "free" we do not mean uncombined with the solvent but only uncombined with the dichloroacetate ion. Therefore we added various amounts of sodium dichloroacetate in addition to that which was regularly produced in the reaction vessel. The effect was large. With increasing concentration of salt the color changed regularly from orange to blue and the rate of reaction increased correspondingly. Now this addition of dichloroacetate does not appreciably affect the activity of the undissociated acid, but it diminishes greatly the activity of hydrogen ion, and it is therefore evident that the orange compound is formed from the blue by the addition of free hydrogen ions.

The question as to whether the orange is produced from the blue substance by the addition of one hydrogen ion or more seems to be decided by our experiments on the rate of fading at different concentrations of dichloroacetic acid. If we assume here, as in our other cases, that the rate of

fading is proportional to the product of the concentrations of blue ion and of the acid, then it is evident that if only one H^+ is required to change the blue substance to the orange, the rate of the reaction could not be diminished by increasing the acid concentration. In fact, however, the rate is diminished. In going from 0.003 M $CHCl_2COOH$ (where the color is not quite pure orange) to 0.03 M , the rate decreases about threefold. We conclude therefore that our orange substance does not correspond to formula IV, but rather to a formula such as V with either two or three hydrogen ions attached to the nitro groups. Attempts to find direct proof of the existence of the intermediate pale or colorless substance failed, and this may indicate that it exists over a very narrow range of H^+ concentration. This would not be surprising, for IV is a less resonating form lying between the strongly resonating forms III' and V, as in the numerous similar cases discovered by Schwarzenbach.²

Turning now to monochloroacetic acid we find at corresponding concentrations very much less of the orange compound and much faster fading. When the acid is at 0.0015 M the solution appears to be pure blue. Making allowance for the smaller specific absorption of the orange substance, it would be hard to believe that this solution contains more than 10–20% of the orange. Therefore its rate of fading should be nearly as high as if the substance were all blue. This proves to be very far from the case. If to this solution, which already contains a small amount of chloroacetate ion, we add lithium chloroacetate (the sodium salt being peculiarly insoluble) we find a great increase in the reaction rate. When the salt is at 0.015 M the rate has increased threefold and is then unaffected by further addition of the salt. The values so obtained are used in Table I. Although these measurements should be extended and quantitative studies of the absorption spectrum made, at present the simplest explanation of these facts is that in addition to the blue and orange the colorless form is present which, compared to the blue, is relatively unreactive.

The Fading of the Orange Compound

The behavior of the orange compound, which we have identified tentatively with formula V, is not our immediate concern. However, some

(1) Kraus, "The Properties of Electrically Conducting Systems," The Chemical Catalog Co., New York, 1922, p. 185.

(2) Schwarzenbach, Ott and Hagger, *Helv. Chim. Acta*, **20**, 498 (1937).

study was made of the rate of its conversion into trinitrotriphenylmethane. This rate proves to be strictly unimolecular with respect to the orange substance and entirely independent of the acid concentration. It is, moreover, the same for hydrochloric and trichloroacetic acids.

The rate is, however, extremely sensitive to water content and this effect is in the opposite direction to the one found with the blue ion. The rate increases with water concentration more rapidly than that concentration itself. Thus at -34° with 2, 3 and 6% water (by volume) the times required to reach the same color standard were, respectively, 360, 135, and 41 seconds.

Since this phenomenon was not investigated further, any explanation must be provisional, but we suggest the following. Since the transfer of an electron pair to the central carbon, forming a primary base at that point (as in formula III), becomes less and less probable as hydrogen atoms are added at the nitro groups, such a configuration occurs too rarely to permit the direct addition of hydrogen ion at that point to contribute appreciably to the reaction rate. On the other hand, the hydrogens on the nitro groups are too far removed from the central carbon to permit a direct rearrangement. If, however, we imagine a chain of water molecules attached at one end to one of the hydrogens of formula V while the other end may come in contact with the central carbon, such a chain might act as a resonating system which could remove hydrogen from the nitro group and add it to the central carbon *as a single act*. This is entirely analogous to the explanation of the very high mobility of hydrogen ion in water, namely, that hydrogen ion is added at one end of a water chain while another hydrogen ion can be removed at the other end. This peculiar mobility of hydrogen ion, although very much smaller, is still present in alcohol solutions, and we may therefore, by analogy, suppose that our rearrangement, although slow, would still exist, even in completely dry alcohol.

Summary

Trinitrotriphenylmethide ion was expected and has proved to be a secondary base. In alcohol when this blue ion is added to any weak acid at

temperatures between -30 and -80° the formation of the corresponding methane is slow and can be followed colorimetrically. The rate of neutralization was studied with numerous acids and under like conditions the rates diminish with diminishing acid strength. With the weakest acids the rates are not proportional to the concentration of acid, and this fact is explained. With the six acids of intermediate strength the rates were found proportional to the concentrations of blue ion and of un-ionized acid, and unaffected by neutral salts. In these cases the heat of activation was calculated from the temperature coefficient of the rates and was found approximately constant with a mean value of 9.1 kcal. By indirect methods the rate of neutralization by alcohol itself was determined. Here the heat of activation is found to be 8.9 kcal. The constancy of the heat of activation over the great range from chloroacetic acid to alcohol can hardly be explained by the theory of an activated complex. The value obtained is taken as a measure of the difference in energy between the primary and secondary forms of the base. The small departures from this constant value are attributed in part to experimental error, but especially to differences in the actual composition of the reacting ion. Several kinds of evidence are adduced to show that the actual composition of the blue ion depends not only upon the solvent but in several cases upon the presence of other solutes.

While the trinitrotriphenylmethide ion is a secondary base with respect to addition of acid to the central carbon, it is a primary base with respect to addition of acid to the nitro groups. In the presence of strong acids an orange substance is thus formed which contains more than one free hydrogen ion per molecule. The very slow rate of fading of the orange compound is studied, and an explanation is suggested for the large catalytic effect of water. Mono- and dichloroacetic acids give mixtures of the orange and blue substances and the rate of fading in these solutions leads to some of the conclusions already mentioned.

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