where the factor 0.3 arises from the fact that there are three equivalent charges of 0.1 each on each methyl group. $E_0 - E_{4f}$ is the difference in energy of the $4f$ and normal states and is about equal to the ionization potential or 10-12 electron volts. The functions $\psi_{2i\sigma}$ and ψ_{4f} were chosen to be hydrogen-like and are given below. The effective nuclear charge equal to three

$$\psi_{2i\sigma} = Are^{-1/2 r/a_0} (1 + \sqrt{3} \cos \Theta)$$
$$\psi_{4f} = Br^3 e^{-3/4 r/a_0} \Theta_{33} \Phi_{3 \cos \varphi}$$

is approximately that obtained by application of Slater's[40] rules for the screening constants of atomic orbitals. A and B are normalizing factors, and $AB = (2.45 \times 10^{-2})/\sqrt{\pi}$. The phase of $\Phi_{3 \cos \varphi} = (1/\sqrt{\pi}) \cos 3\varphi$ was so chosen that the hydrogen atoms lie in the planes $\varphi = 0$, $\pi/3$ and $2\pi/3$ corresponding to the maximum values of $\Phi_{3 \cos \varphi}$. The term $1/r_b$ was expanded in terms of spherical harmonics about the center of the carbon atom. Due to orthogonality, all terms integrate out except those involving the harmonics $\Theta_{33}\phi_3 \cos \varphi$ and $\Theta_{43}\phi_3 \cos \varphi$. The result is that $0.3 \int \psi_{2i\sigma} e^2/r_b \psi_{4f} d\tau = 1.56 \times 10^{-2}$ e. v. and the coefficient of the $4f$ function is correspondingly about 1.5×10^{-3}. This coefficient is, as we see, so small that no appreciable contribution to the barrier can come from this cause, in agreement with our earlier result and in disagreement with Eucken and Schäffer. The barrier therefore arises from other causes such as are considered in this paper.

(40) Slater, *Phys. Rev.*, **36**, 57 (1930).

We wish to express our appreciation to Drs. William Baker and John Beach for helpful discussions.

Summary

1. The problem of restricted rotation about the C–C bond in ethane is discussed. It is shown that the repulsions between the hydrogen atoms cannot account for a barrier of 3000 cal. The effect of the distortion of the spherical symmetry around the carbon atoms by the perturbations of the hydrogen atoms is considered. It is shown that this effect tends to make the opposed form more stable but also cannot account for a barrier of the required height. The effect of resonance with double bonded structures is then considered and it is shown that with reasonable assumptions concerning the angular dependence of the exchange integrals between carbon orbitals, the opposed structure is the stable one with a barrier height of 0.7 to 1.9 kcal. If we add to this the effect of the dissymmetry of the carbons a barrier of the right order of magnitude is obtained.

2. It is shown that this effect of resonance with double bonded structures can be used to explain the alternation in physical properties such as melting points of long chain compounds.

3. The experimental evidence in favor of the staggered or opposed structures for long chain and cyclic compounds is discussed.

Primary and Secondary Acids and Bases

BY GILBERT N. LEWIS AND GLENN T. SEABORG

The most general classification[1] of bases and acids does not extend the class of bases much beyond the group of substances now recognized under that name. On the other hand, if we define an acid as any substance one of whose atoms is capable of receiving into its valence or coördination or resonance shell the basic electron-pair of another atom, then we have a great group of generalized acids in which the hydrogen acids are not the strongest and not always the most typical members.

The self-consistency of this group of generalized

(1) Lewis, "Valence and the Structure of Atoms and Molecules," Chemical Catalog Co., New York, 1923, p. 142.

acids has been brought out in a recent paper[2] which emphasizes the extraordinary similarity in every type of behavior, extending even to the colors of their compounds with indicators, between hydrogen acids and all the other acids of the class. All the acids can be ranked roughly by their strengths. Thus, for example, sulfur dioxide is ordinarily weaker than hydrochloric acid, which in turn is much weaker than boron trifluoride or stannic chloride. Aside, however, from these considerations of relative strength, there was proposed in that paper an entirely independent classification into *primary* and *secondary*

(2) Lewis, "Acids and Bases." *J. Franklin Inst.*, **226**, 293 (1938).

acids and bases which, as far as we can now see, probably represents a difference, not of degree, but of kind.   It was assumed that there is a large group of acids and bases, called primary, which require no energy of activation in their mutual neutralization, but that apparently there is another group, called secondary, such that a secondary acid does not combine, even with a primary base, nor a secondary base with a primary acid, except when energy, and frequently a large energy of activation, is provided.

It is to be presumed that an acid which conforms to the defintion of our first paragraph is primary and that when a heat of activation is found to be necessary, it means that some change in the condition or structure of the molecule is needed to make it conform to that definition. Frequently we can see in advance that such a change is necessary.   For example, an isolated molecule of an acid might be primary, but when dissolved in a basic solvent may be completely neutralized by forming a complex with the solvent, which would have to be dissociated before the acid could combine with some stronger base. We should then expect a heat of activation which may be smaller, but cannot be larger, than the heat of dissociation of the complex.   In other cases a known structural change must occur, as, for example, in the change from a keto to an enol form, before a substance shows marked acid properties.   Such a substance has been called by Hantzsch[3] a pseudo acid.

The Possibility of Electromerism

Such cases of secondary acids and bases as we have just mentioned, in which the acid or basic properties appear only after the breaking of some bond or the rearrangement of the atoms within a molecule, are familiar.   We are going to see, however, that there are numerous secondary acids and bases which do not appear to conform to these specifications of what we may call the classical type.   The explanation of the behavior of these substances is a perplexing and at present an unsolved problem.   There is one possible explanation which must be considered.

A quarter of a century ago many chemists hoped to find isomers of the type called *electromers*, that is, two forms of a molecule with the atoms in the same, or nearly the same, relative position, but with a difference in electronic dis-

(3) Hantzsch, *Ber.*, **32**, 575 (1899).

tribution.   The advent of the electron-pair bond and the associated idea of the mobility of this bond under inductive influence seemed to make assumption of such electromers superfluous in the case of simple molecules.[4]   Moreover, the development of the concept of resonance has appeared to exclude electromerism in all cases except the trivial one in which two parts of a molecule are so far insulated from one another that they behave like separate molecules.

When in a given substance there is said to be resonance between two or more limiting structures, the phenomenon is most marked when there is little difference of energy or of spacial position in the resonating structures, but we assume that even when these conditions are not fulfilled there will be some resonance effect, although perhaps minute.   On the other hand, there are structures which we must believe are prohibited from any mutual resonance whatsoever.   Such a prohibition occurs when one of the structures is paramagnetic and the other diamagnetic.   In other cases, even when spins are not considered, the quantum mechanical equation sometimes has two sets of solutions which are not mutually "combining."   A structure representing one set and a structure representing the other should be incapable of mutual resonance, and therefore should behave as true electromers.   We are going to consider the electromeric hypothesis as a possible method of accounting for the sharp distinction between primary and secondary acids and bases, although we are by no means convinced that this is the only possible way of accounting for the phenomena that we shall describe.

Some Secondary Acids and Bases

In our still mysterious group of secondary acids the most familiar one is carbon dioxide.   It has long been known that a cold aqueous solution of carbon dioxide cannot be titrated instantly with alkali.   By using another solvent and lower temperature this phenomenon can be rendered more striking, as shown in the experimental section. Among organic substances with the carbon–oxygen double bond it seems likely that the acid chlorides and the acid anhydrides will in general prove to be secondary acids.   By analogy it was thought that compounds containing the carbon–carbon double bond might show secondary characteristics, and several compounds of this type

(4) Lewis. "The Atom and the Molecule," THIS JOURNAL, **38**, 762 (1916).

will be discussed in the experimental section. None of the latter proved to be secondary acids or bases.

Another large group of secondary acids is found in the triphenylmethyl cation and its many derivatives. Such ions as those of crystal violet and malachite green combine slowly with hydroxide ion to form the carbinol, and the heat of activation is large. Even triphenylmethyl chloride in chlorobenzene is partly ionized and when circumstances produce a recombination of the ions this process is a slow one, especially at 0°, as shown in the preceding paper.[2]

Before considering the problem of secondary bases let us consider for a moment the class of substances which in a sense is intermediate between acids and bases, namely, the odd molecules. It has been supposed that the union of two odd molecules should not require activation energy. This supposition, moreover, was supported by experimental observations. Thus nitric oxide and oxygen, in both of which there are odd electrons, combine instantly at the temperature of liquid air. However, it has been discovered by Ziegler[5] that two molecules of triphenylmethyl require an activation energy of 6-8 kcal. when combining to form one molecule of hexaphenylethane. We shall try to explain this interesting fact by assumptions entirely similar to those which we are going to make in interpreting the behavior of the triphenylmethyl cation.

The question now arises as to whether we can find any secondary bases. By analogy to the compounds we have just been discussing it seemed likely that the negative triphenylmethide ion might prove to be such a substance. This ion itself is not very convenient to study, but it has long been known that 4,4',4''-trinitrotriphenylmethane behaves as a weak acid. It dissolves in alkaline alcohol to give an intense blue color which is due to the substituted triphenylmethide ion, the investigation of which we describe in the paper immediately following. There we show that this ion is truly a secondary base since at low temperatures it is neutralized slowly by a wide variety of acids, the heat of activation in each case being approximately 9 kcal.

The only other group of secondary bases which is now known to us was called to our attention by Professor Branch. Nitromethane and many of its derivatives form salts in alkaline solution and

(5) Ziegler, Orth and Weber, Ann., 504, 131 (1933).

the anions thus produced are only slowly neutralized by weak acids to give back the nitromethane. The general course of this process of neutralization, even to the inhibiting effect of strong acids, is so similar to the behavior of the trinitrotriphenylmethide ion that a common explanation is strongly suggested.

Let us now consider how we should regard triphenylmethyl and its ions if we are to adopt the electromeric hypothesis. In the accompanying graphical scheme formulas I, II and III show what may be called the old-fashioned representations of the triphenylmethyl cation, the triphenylmethyl free radical and the trinitrotriphenylmethide anion. In each of these the central carbon has only three bonds and the formulation indicates that the central carbon is the seat of the respective behaviors as acid, odd molecule and base.
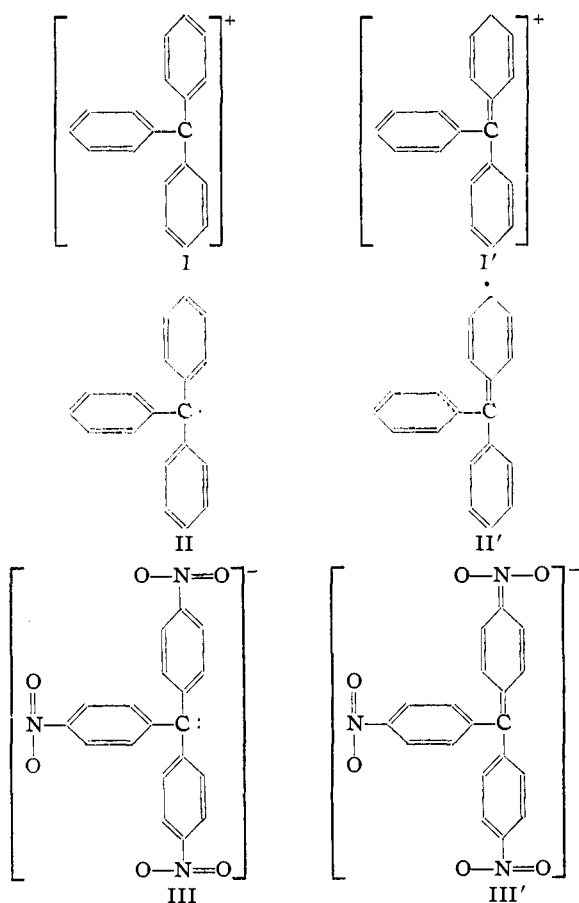
The formulas I', II' and III' represent, somewhat inadequately, the resonance structures which we now believe to characterize these molecules in their normal state. Formula I', for example, exhibits but one of the nine structures which almost

equally contribute to the resultant resonance state. Thus the central carbon may be doubly bonded to any one of the three phenyl groups and any one of the ortho or para carbons may be regarded as possessing the acid character and the positive charge. Similarly in II′ the odd electron may be placed upon any one of nine carbon atoms. In formula III′ the basic property is to be equally distributed among the three nitro groups.

The structures on the left in our scheme have heretofore been assumed to contribute to a greater or less degree to the general resonating molecule. We are now suggesting the possibility that they do not contribute to any degree whatsoever to the molecule in its normal state. According to this hypothesis we may have in solution two distinct substances, each with its own properties, and, if the two are in equilibrium with each other, their relative concentrations will depend chiefly upon the temperature and upon the difference in their energies. Each member of an electromeric pair must be assumed to have not only its own physical properties, such as color, but also its specific chemical properties. It is by the latter that we may ordinarily expect to detect the existence of the two forms. Thus, for example, each of the two forms II and II′ is an odd molecule, but the first will combine instantly with another odd molecule at the central carbon atom. So two molecules of II will combine instantly to form hexaphenylethane, while two molecules of II′ can combine without activation only to form another dimer in which two phenyl groups are directly attached. It seems probable that such a dimer exists in small amount, in rapid equilibrium with the monomers, in any system containing such free radicals.

Similar conditions are to be assumed in the case of the trinitrotriphenylmethide ion. In form III the central carbon should behave as a typical primary base. When we go over to the more stable ion III′ the basic character has not been lost, but the pair of electrons, which was on the central carbon, is now resonating chiefly between the three nitro groups. If, therefore, a strong enough acid is added to the blue ion, we should expect hydrogen ion to add, and add instantly, at one of these positions. This is one of the phenomena which will be described in the paper immediately following. The fact that a substance may act as a secondary acid or base with respect to neutralization at one point in the molecule and at the

same time behave as a primary acid or base with respect to some other point of neutralization must be constantly borne in mind.

Unless the distinction between primary and secondary acids and bases is a fundamental one, it would be expected that the number of slow neutralizations, which have been observed in the neighborhood of room temperature, would rapidly increase as we study reactions at successively lower temperatures. We shall see, however, in our experiments which were carried out progressively at lower and lower temperatures, until finally numerous experiments were made at $-160°$, that not a single case was found of a secondary acid or base, except those already listed.

Other Possible Explanations

At present we have no definite clue as to the origin of the distinction between secondary and primary acids and bases. Neither are we able to predict, except by analogy to other substances of a similar sort, when we may expect to find substances of the secondary type. One suggestion is worth serious consideration. In the case of each secondary acid or base that we have found, the process of neutralization causes a notable change in the geometry of the molecule. Thus CO_2, which is linear, becomes a planar structure when it adds to OH^-. In triphenylmethyl ion, the central carbon, and the three phenyl carbons to which it is attached, are presumably coplanar, but when the ion adds OH^- or Cl^- a tetrahedral molecule results. If our trinitrotriphenylmethide ion is completely representable by formula III′, once more the central atom and the three attached carbons should be coplanar. On the other hand, if it were all in the form III, it should be tetrahedral like ammonia. If both forms were in resonance together, then we should expect a slightly pyramidal form, the departure from coplanarity being dependent upon the contribution that formula III makes to the resonance state.

Is the activation energy which is required in the neutralization of secondary acids and bases to be regarded as a consequence of these important changes in the geometry of the system? Our present answer is in the negative, chiefly because of two experiments which will be described and which were designed expressly to test this point. The strong acids boron trichloride and trifluoride are in all probability completely planar, like triphenylmethyl ion, and go over into tetrahedra

when a base is added. It therefore seemed important to ascertain whether these acids show any signs of secondary behavior. We shall see that they both behave as primary acids and are neutralized instantly (within a fraction of a second) even at the extremely low temperature $-160°$. As an even closer analog to triphenylmethyl ion it would be interesting to study the rate of neutralization of the acid triphenylboron.

The only remaining alternative to the electromeric hypothesis that has occurred to us is that when a substance acts as a secondary acid or base with respect to neutralization at a certain point in the molecule, this point is covered and protected, either by some chelation in the molecule itself, or by some hitherto unsuspected type of combination with the solvent or other solute molecules. We have pointed out the great similarity between our new secondary base and the anion of the derivatives of nitromethane. In the new edition of Sidgwick's "Organic Chemistry of Nitrogen"[6] there is a very full discussion of the various structures of such an ion which have been suggested to account for the observed properties, especially the retention of optical activity. It is there pointed out that no one of these structures appears to be satisfactory. It is our opinion that the observed properties of nitromethide ions are not those of any substance which can be expressed by a formula which ignores a complex with the solvent, and indeed if a solvent could be found which does not form such complexes, the properties of the ion would be entirely different. Assuming now one or more molecules of the solvent, usually alcohol, attached to the simple ion, such molecules might conceivably form such a chelated system as to protect the methide carbon from immediate attack. The process of activation would then consist in breaking the attachment. Moreover, as our studies have progressed, we have found numerous examples of the formation of peculiar complexes with solvent molecules of the type which might conceivably lead to such protection of an atom as to prevent its action as a primary acid or base. Nevertheless, after considering all the cases now available, and especially the simplest and most typical case of carbon dioxide in water or alcohol, we regard the electromeric hypothesis as the most probable explanation of our phenomena.

Whatever the explanation may be, our immedi-

(6) Sidgwick, Clarendon Press, Oxford, England, 1937.

ate purpose must be to substantiate the idea that a secondary acid or base exists in two different forms, in only one of which neutralization at a given point proceeds rapidly and without activation.

Kinetics

Recognition of the distinction between primary and secondary acids and bases leads to certain kinetic considerations which were implied in the preceding paper[2] and which we must now subject to careful analysis. We are going to discuss two theses, neither of which can be regarded as proved, but both of which have become increasingly plausible as our experiments have proceeded.

Thesis I.—The first thesis, which is a direct consequence of our assumptions, is that in the neutralization of a secondary acid or base the rate of the reaction will frequently be determined, either by the rate of formation of the primary form from the secondary form, or by the concentration of the primary which is in equilibrium with the secondary form.

Let A be any primary acid and let B_S be the ordinary state of a secondary base, whose primary form, of higher energy, may be called B_P, and let us consider the following sequence of reactions

$$B_S \longrightarrow B_P \qquad B_P + A \longrightarrow BA \qquad (1)$$

We may first consider the case in which the first step is slow compared with the second; in other words, the first is the rate determining process. This rate of forming B_P from B_S will be given by an expression of the Arrhenius form in which the coefficient involves probabilities, and the exponent contains the heat of activation q, which is the difference in energy between B_P and B_S. As long, therefore, as the first step is rate determining, the rate of the reaction, at each temperature, will be independent of the concentration and of the nature of A. If this case can be realized experimentally, under conditions which permit no misinterpretation of the experiments, we shall have the most direct proof of our assumptions. We have not yet found a case of this sort.

Let us next consider the case in which the second step of reaction (1) is much slower than the first. Then B_S and B_P are in equilibrium, so that (ignoring differences in entropy) c_P/c_S, the ratio of the two concentrations, is proportional to exp. $(-q/RT)$. If then the reaction is bimolecular with respect to acid and B_P, it is also bimolecular with respect to acid and B_S. Once more q will be

the heat of activation. Therefore according to our assumptions we may expect to find in reactions of this type a heat of activation which is often independent of the nature of the acid.

Ordinarily it would be assumed that the process that we are considering would occur, not as represented in mechanism 1, but by the mechanism of the activated complex. According to the latter view a molecule of B_S and a molecule of A occasionally would collide with sufficient energy so that in a single step the combined system could pass over some potential barrier to produce the stable molecule BA. With a given base the height of the barrier and therefore the heat of activation would vary with the nature of the acid. According to our view also this would be the mechanism if an acid were found for which the barrier that we have just mentioned is lower than the difference in energy between B_S and B_P. Supposing, for example, that this barrier were proportional to some inverse function of the strength of the acid, then according to the theory of the activated complex, the heat of activation found for different acids would be expected to fall upon line I of the schematic diagram, Fig. 1. On the other hand, according to our view, the experimentally found heat of activation might follow the same line up to a point, but from that point on the values would be constant (line II). This would be approximately the point at which the height of the barrier of the activated complex would begin to exceed the heat of activation of mechanism 1, namely, E_P-E_S.

In the following paper we show that in the neutralization of trinitrotriphenylmethide ion the heat of activation is essentially constant with acids covering the great range from chloroacetic acid to ethyl alcohol. In other words all these cases seem to fall on the horizontal line (line II) of Fig. 1. It would seem almost impossible to interpret these results by the theory of the activated complex.

Thesis II.—The second of our main theses is much wider in its scope, since it concerns, not the rarer cases of the secondary kind, but rather all molecules of the resonance type. When a substance is said to resonate between several structures, then, if the energy calculated for one of the structures is very much larger than that for the actual substance, that structure is said to contribute very little to the actual state of the substance. The question however is one of degree
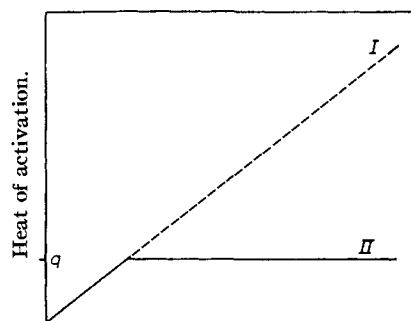
Some inverse function of acid strength.
Fig. 1.

and we may assume, except when there is an absolute prohibition of resonance such as we have been discussing, that all possible electronic structures, no matter how small their contribution, must be regarded as members of the resonance family.

It has been assumed that if a resonating molecule reacts in a way which could only be interpreted as a behavior peculiar to one of the contributing structures, and if this structure is one of high energy, then such a reaction must require a heat of activation corresponding roughly to the difference between the normal energy of the molecule and the energy calculated for that particular structure.[7] Just the *opposite* of this assumption is the one we are now going to propose as our second thesis.

Let S be any resonating molecule in its state of lowest energy, and let S_1, S_2, . . . be individual structures which may be said to contribute to the actual molecule S. Let E be the actual energy and E_1, E_2, . . . the higher energies calculated for the hypothetical individual structures. Now we are going to assume that, to permit a reaction characteristic of the form S_1, we do not require an activation energy of the order of E_1-E but that the process *may* occur without any activation no matter how large this energy difference is. With respect to heat of activation, the difference between a set of tautomers and a set of resonating forms may be expressed as follows. A tautomer can be converted into another tautomer of higher energy only when the requisite energy is obtained from an external source; on the other hand, a resonating molecule, even when isolated, may be said to pass through its various phases, some of low energy and some of high, by processes which were forbidden in the old mechanics but permitted in the new.

(7) See for example Anderson, *J. Chem. Soc.*, 1042 (1936).

What we have said pertains to the exponential part of the Arrhenius expression for reaction velocity. Does the coefficient of this expression, which depends, in the case of a bimolecular reaction, upon the probability that each collision is effective, vary greatly with the extent to which the structure S_1 contributes to the general resonance state S? We have at present no answer to give to this question except for the following remark.

It is occasionally convenient to consider that in a resonating molecule there is a rapid oscillation in the electron cloud so that the system approaches now one, now another, of the particular structures such as S_1, S_2, ... If we take this view we have to consider, not only what fraction of the time the molecule can react as though it were in the form S_1, but also how frequently this state or phase recurs, or, in other words, the resonance frequency. In the case of a gaseous collision the duration of the collision is presumably of the same order of magnitude as the resonance time. In such a case the chance of an effective collision might depend very greatly upon whether the reacting form is a major or minor constituent of the resonating molecule. On the other hand, in a liquid, if two molecules come together, they probably remain together for a considerable time, during which a resonating molecule may pass many times through its various phases. In such case it would appear that the probability of effective collision would not depend very greatly upon the extent to which the reacting form contributes to the resonance state. As a matter of fact the experiments we are to describe are consistent with the latter supposition.

When we apply our second thesis specifically to acids and bases we find the following consequences. When one of the contributing structures of a resonating substance, no matter how small the contribution may be, has the form of an acid or a base, the substance will behave as a primary acid or base, and when it combines with any primary base or acid it will do so without activation. There is no connection whatsoever between the ability to act as a primary acid or base and the acid or basic strength. All of the substances of secondary type that we have found have been moderately strong acids and bases. On the other hand, we are going to describe experiments with extraordinarily weak bases which do not combine to any appreciable extent except with the very strongest acids; but insofar as the process of neutralization occurs, it occurs instantly, even at very low temperatures.

Some of the bases that we have used in our experiments have ionization constants which we estimate to be as low as 10^{-22} and a very rough calculation of $E_1 - E$ in such a case would give something like 20–30 kcal. Nevertheless our experiments show that such bases are neutralized within a fraction of a second at $-160°$. Considering the dilution of our solutions, we may state that the

heat of activation, if it exists at all, cannot be greater than 4 kcal.

Experiments

Carbon Dioxide as a Secondary Acid.—If at $-60°$ we dissolve carbon dioxide in alcohol and divide the solution equally between two tubes, A and A′, and if at the same temperature we have an alcohol solution containing dilute sodium ethylate and a little indicator, such as brom cresol purple, divided equally between the two tubes, B and B′, then if A is added to B at once there is no immediate change of color. However, on standing for some fifteen minutes the carbon dioxide neutralizes the ethylate ion and the indicator passes slowly through its color changes. If now, having stood for half an hour or so, the contents of A′ are added to B′, the indicator goes at once to the acid color. We have not yet ascertained whether the time required to produce the acid color is the same in the two cases.

The latter of these experiments, which shows that the solution of carbon dioxide in alcohol only slowly becomes an acid, might conceivably, although improbably, be explained on the assumption that the oxygen of C_2H_5OH adds immediately to the carbon of CO_2 but that it takes time for the hydrogen to pass over to one of the oxygens of the CO_2, producing the ordinary ethyl ester of carbonic acid. However, the former experiment shows the falsity of this explanation. In that case the basic ion $C_2H_5O^-$ can add directly to the carbon of CO_2 to give the final stable product. The fact that it does not do so immediately at low temperatures shows that a heat of activation is necessary, or in other words, that carbon dioxide is a secondary acid.

Methods of Studying Reactions with Indicators at Very Low Temperatures.—Numerous experiments were made with reactions at a variety of low temperatures, but since these were all repeated at our lowest temperature, with identical results, we shall proceed immediately to describe a series of experiments made at $-160°$ (113°K.). As far as we are aware, this is the lowest temperature at which chemical reactions have been observed except in the case already cited of the instantaneous union of the two odd molecules NO and O_2 at 90°K. At the temperature of $-160°$ we may be sure that if any instantaneous reaction has any heat of activation at all it cannot be greater than about 4 kcal. To obtain any evidence for a smaller heat of activation than this it will be necessary to use indirect methods, of which several are available, but which we have not yet tried.

The experimental method first used was extremely simple. The acid or base to be tested was dissolved in petroleum ether of freezing point $-160°$. This was placed in a flask which could be attached to the vacuum line by a ground-glass joint. The solution was then frozen and the flask exhausted. The contents were then melted and in order to get rid of the small amount of air remaining, the process of freezing and exhausting was repeated. The connection between the flask and line now being closed by a stopcock, the line, comprising about 50 cc., was filled with the vapor of the base or acid to be used for the neutralization, at a pressure of about 10 cm. The liquid air, which had been used for freezing, was now

removed and the solution in the flask was agitated by a small piece of iron enclosed in glass which had been placed at the bottom of the flask and was now moved by means of a small permanent magnet held outside the flask. When the contents of the flask were about half melted the experiment was performed by opening the stopcock. When the vapor is such as produces a color change, then at the instant at which the vapor impinges upon the surface of the solution the color appears. This color then spreads through the solution, soon after which sometimes a colored precipitate forms. The time from opening the stopcock to appearance of bright color is not more than a few tenths of a second.

Although the amount of vapor entering the flask is very small, it seemed possible that the surface temperature might be raised appreciably by it. Therefore the more crucial experiments were repeated in a new apparatus in which constancy of temperature was assured. This apparatus was attached to the vacuum line by a horizontal ground glass joint. In a plane perpendicular to the axis of the joint an inverted Y-tube could be rotated so as to mix and stir the contents of the tube. With acid in one limb and base in the other, each dissolved in petroleum ether, the whole was immersed in a large bath of half-frozen petroleum ether. When completely cooled the apparatus was then rocked and as the liquids mixed an instantaneous color change was observed. Observations with the two types of apparatus were in every case identical. All the following experiments were made at $-160°$ and in petroleum ether as solvent.

Boron Trichloride as an Extremely Strong Primary Acid.—When boron trichloride was added to a solution of butter-yellow there formed instantly the pure red which is characteristic of the compounds of this indicator with all acids, whether of the hydrogenic or the non-hydrogenic type. Within a few seconds a red precipitate was formed. This experiment proves that boron trichloride, in spite of its geometrical resemblance to triphenylmethyl ion, is a primary acid, at least if we decide for the present to call all acids and bases primary which are neutralized instantly at $-160°$. Incidentally this experiment shows also that butter-yellow is a primary base.

Boron Trifluoride as an Extremely Strong Primary Acid.—The previous experiment was repeated with boron trifluoride instead of boron trichloride. The result was the same, showing that boron trifluoride is a primary acid. It is generally assumed that boron trifluoride is on the average a stronger acid than boron trichloride, but as far as our experiments have gone this idea is not confirmed. Since, moreover, boron trifluoride is in general more destructive to organic substances than boron trichloride, the latter has been used in the majority of our further experiments.

Trinitrobenzene and Trinitrotoluene as Weak Primary Acids.—These two substances stand alone among common indicators in that their acid behavior is not due to giving up hydrogen ion, or forming a hydrogen bond, but is due to the direct addition of a base. When solutions of these two substances are treated with ammonia gas at our lowest temperature they at once change from colorless to bright red. The reason that ammonia was used in this experiment, rather than a stronger base such as diethylamine,

we shall discuss in another paper. Incidentally this experiment shows that ammonia is a primary base.

Dibenzalacetone and its Analogs as Very Weak Primary Bases.—Dibenzalacetone, dipiperonalacetone and dianisalacetone give in concentrated sulfuric acid strongly colored solutions, orange, purple and red, respectively. Their relative basic strengths in this solvent were estimated through the method of Baeyer and Villiger by Stobbe and Haertel,[8] who found that the basicity increased in the order listed. We find that they are all stronger bases than acetone, although the difference is not great in the case of the first substance; for in this case the gradual addition of acetone to the colored solution in 95% sulfuric acid destroys the greater part of the color. When these three substances are dissolved in concentrated aqueous hydrochloric acid the first shows only the yellow color characteristic of the uncombined substance, the second gives a pale purple and the last a stronger red. If these substances are dissolved in petroleum ether and gaseous boron trichloride added, the initial colors produced are, as far as can be noted visually, identical with those in sulfuric acid. When boron trichloride was introduced at $-160°$ all three color changes were instantaneous, showing that all three substances are primary bases.

Unsymmetrical Diphenylethylene as a Very Weak Primary Base.—This substance treated with boron trichloride in the usual way at the lowest temperature gave an instantaneous red color. It is therefore, by our present criterion, a primary base. It is a stronger base than the symmetrical compound, stilbene, which is not appreciably neutralized by boron trichloride in petroleum ether. Another base which also proved too weak is diphenyloctatetraene. This last substance, and the other polyene which we are about to discuss, were kindly furnished to us by Dr. M. Calvin. Also the tetracyclic hydrocarbon, perylene which was kindly furnished to us by Professor L. F. Fieser, proved to be too weak a base for our purpose, although in 95% sulfuric acid it is colored.

Symmetrical Diphenyldodecahexaene and β-Carotene as Extremely Weak Primary Bases.—These substances represent the very weakest bases that are appreciably neutralized by boron trichloride in petroleum ether. They both give a blue color in 95% sulfuric acid and an intense blue in fuming acid. They both prove to be primary bases. Carotene at our low temperature gave with boron trichloride an instantaneous blue color, followed in a few seconds by a green precipitate. The diphenyldodecahexaene also gave an instantaneous brilliant color, but instead of the expected blue a brilliant orange appeared. However, upon warming to about $-80°$, the color changed to blue, while the orange color reappeared when the solution was once more cooled. Apparently the compound adds more than one molecule of boron trichloride at very low temperatures.

Summary

Most acids and bases neutralize one another rapidly at all temperatures. These are called primary. Some other acids and bases, called secondary, require heat of activation for the neu-

(8) Stobbe and Haertel, *Ann.*, **370**, 99 (1909).

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.

Trinitrotriphenylmethide Ion as a Secondary and Primary Base

BY GILBERT N. LEWIS AND GLENN T. SEABORG

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 triphenylmethyl 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-

III(B_P?)   III'(B_S?)

IV   V