uid junction potentials by extrapolation has been tested in cells with buffer solutions. Experimental data are presented which indicate that the junction extrapolation is linear as a first approximation.

The method is applied to the determination of the standard potential of the silver electrode at 5, 15, 25, 35 and 45°. Values of ΔS^0, ΔH^0 and ΔC_p^0 have been calculated for the electrode reaction at 15, 25 and 35°.

By combination of the normal potentials of the silver and silver–silver halide electrodes, the solubility products and solubilities of (electrolytic) silver chloride, bromide and iodide have been computed from 5 to 45°. Values of ΔS^0, ΔH^0 and ΔC_p^0 for the reaction $AgX = Ag^+ + X^-$ have been recorded at 15, 25 and 35°.

A self-consistent table of relative ionic entropies and heat capacities from electromotive force data has been made for the silver ion, chloride ion, bromide ion and iodide ion at 15, 25 and 35°.

NEW HAVEN, CONN. RECEIVED JUNE 29, 1938

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

Infrared Absorption Studies. V. Association in the Carboxylic Acids

BY A. M. BUSWELL, W. H. RODEBUSH AND M. F. ROY

The electron conception of valence proposed some twenty years ago led to the prediction in 1920 of two types of associated liquids.[1] In one of these the molecules should be combined with the formation of definite polymers (dimers in the case of acetic acid) while in the other type polymers of indefinite molecular weight and structure were anticipated. Radically different behavior, especially in the case of solvent properties, was predicted in the two cases. The liquids composed of polymers of indefinite molecular weight comprised the typically polar solvents such as water or alcohol, while in those having definite polymer molecules non-polar properties were to be expected.

Since then a great deal of additional evidence has been accumulated to emphasize this difference. For example, acetic acid shows no dipole moment in benzene solution whereas alcohols show an increasing polarization with increasing concentration. Alcohols also form glasses at low temperatures, which have been shown by Zachariasen[2] to involve polymerization with hydrogen bond formation. It is not possible, of course, to anticipate or predict in every case the type of polymer to be expected and that problem is one which still holds the greatest interest. The data from which conclusions could be drawn have been available for a long time; witness the excellent review by Lassettre[3] based entirely upon the ordinary data of physical chemistry. More recently a study of simple solubility by Zellhoefer, Copley and Marvel[4] has yielded a surprising amount of additional confirmatory data along these lines.

The existence of these two types of association has perhaps contributed to the confusion which for many years characterized the attempts of physical chemists to discuss the behavior of the so-called "normal" and "associated" liquids. This confusion was all the more inevitable because it is now obvious that the normal or unassociated liquid lies intermediate in its properties between the two types of associated liquids.

It should be mentioned at this point that a third type of association through hydrogen, namely, intramolecular association or chelation, may occur, which has the result of producing a "normal" behavior in a molecule which would otherwise show abnormal behavior as a liquid and solvent. This type of association has been much studied by Sidgwick[5] and his collaborators. The conditions under which it occurs are well defined, and one of the important ones is apparently the possibility of two configurations of the molecule with respect to the hydrogen, thus giving an opportunity for resonance.

All of the types of association of interest in the liquid state appear to involve hydrogen bonding. The formation of polymers depends upon potential cross linkages or additional valences between

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[1] W. M. Latimer and W. H. Rodebush, THIS JOURNAL, **42**, 1432 (1920).

[2] W. H. Zachariasen, *J. Chem. Phys.*, **3**, 158 (1935).

[3] E. N. Lassettre, *Chem. Rev.*, **20**, 259 (1937).

[4] G. F. Zellhoefer, M. J. Copley and C. S. Marvel, THIS JOURNAL, **60**, 1337 (1938); G. F. Zellhoefer and M. J. Copley, *ibid.*, **60**, 1343 (1938).

[5] N. V. Sidgwick, "The Electronic Theory of Valency," Oxford University Press, 1929.

molecules. In the typical organic polymers these cross linkages are strong and irreversible and lead to the formation of inert solids. Because of the low energies of activation and dissociation of the hydrogen bond, the polymers formed may be liquid or if the unit molecules are large, substances capable of colloidal dispersion as in the case of the proteins may be formed.

While it is possible to determine from a study of the physical data the type of association present, it is not possible to explain or predict such association without more direct information as to the molecular structure. The first important advance in this type of study was made by Pauling and Brockway[6] when they confirmed the prediction of Latimer and Rodebush, showing by means of electron diffraction that the dimer of formic acid has a symmetrical ring structure involving both carboxyls. The methods of electron diffraction do not, of course, lend themselves to the study of solutions and a further great advance was made when Wulf[7] and his collaborators began the study of the infrared absorption of organic substances in an inert solvent. They noted the absence of the second harmonic in the case where hydrogen bonding, particularly of the chelated type, was to be anticipated.

After the work of Wulf and his collaborators came to our attention, experiments were begun in this Laboratory[8] upon the infrared absorption of certain types of compounds in which hydrogen bonding was present. We investigated a large number of compounds in the region where the fundamental of hydroxyl was to be expected and found the very important generalization that the formation of a hydrogen bond is accompanied by a very considerable increase in the absorption and a marked change in frequency, the shift being in the direction of longer wave lengths. This work has been amply confirmed by other investigators working independently,[9] at least in the case of polymerization. So far as we know, we were the first to call attention to the shift in absorption accompanying the formation of an intramolecular hydrogen bond. In previous publications we have reported the investigation of the shifts in the fundamental frequency of a considerable variety of compounds, following more or less the lines laid down by Wulf and his collaborators in their investigation of the harmonic absorption. In the present paper we wish to report results which have to do mainly with association and which include the formation of hydrogen bonds where the hydrogen is linked to atoms other than oxygen and, in particular, the formation of hydrogen bonds between different types of molecules, a subject which is of the greatest interest and which has not been studied to any considerable extent.

Hydrogen bonds are known to be formed readily when hydrogen is attached to nitrogen, oxygen and fluorine. Certain types of compounds such as ether hydrochloride and chloroform–ether suggest that carbon and the other halogens should be included in the list. It is certain that for bond formation the hydrogen must be active to some degree, which means, of course, ionizable in the proper solvents. Hydrogen attached to carbon in an ordinary hydrocarbon is incapable of forming a bond; likewise apparently there is little tendency for the hydrogen of ammonia of the amines to form bonds. All the physical properties of the amines indicate[10] the lack of association and our infrared studies do not indicate any bonding in the case of aniline for example. On the other hand, the hydrogen of chloroform shows a strong tendency toward bonding, even with the oxygen of ether. The question as to whether the hydrogen of chloroform is more "active" than the hydrogen of an amine, such as aniline, is one to which it is difficult to make an answer. Data upon the ionization constants must be applied in non-polar solvents with a good deal of caution. Certainly our conclusions show that the hydrogen of chloroform and all the hydrogens which are more active will form hydrogen bonds either with another molecule of the same kind or with one which is perhaps more basic. There seems to be no evidence, for example, that hydrogen chloride is associated but the ether hydrochloride complex is a clear case of hydrogen bonding. On the other hand, moderately acidic substances such as the amides or carboxylic acids show a very strong tendency toward association.

One important generalization that has been suggested by Venkateswaran[11] from a study of the Raman and infrared spectra appears to be con-

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[6] L. Pauling and L. O. Brockway, *Proc. Nat. Acad. Sci. U. S.*, **20**, 336 (1934).

[7] G. E. Hilbert, O. R. Wulf, S. B. Hendricks and U. Liddel, This Journal, **58**, 248 (1936).

[8] A. M. Buswell, V. Deitz and W. H. Rodebush, *J. Chem. Phys.*, **5**, 84, 501 (1937).

[9] J. Errera and P. Mollet, *Nature*, **138**, 882 (1936); J. J. Fox and A. E. Martin, *Proc. Roy. Soc.* (London), **A162**, 419 (1937).

[10] W. D. Kumler, This Journal, **57**, 600 (1935).

[11] C. S. Venkateswaran, *Proc. Indian Acad.*, **7**, 13 (1938).

firmed here. When a bond is formed, the more acidic the hydrogen, the greater the shift in frequency toward the longer wave length and the broader the resulting absorption band. The foregoing statement applies to the stretching frequency. Our evidence on the bending frequency is limited to the case of chloroform, and since there is possibly some uncertainty concerning it, we will discuss the behavior of the bending frequency in connection with the experimental work on chloroform compounds in a subsequent paper.

The question as to the strength of the bond formed between various types of molecules is one upon which we have only qualitative evidence. Qualitatively, the bond strengths appear to be all of the same order of magnitude. This can scarcely be true, but a study of the heats of mixing under various conditions would be very desirable.

In the foregoing discussion we have tacitly assumed that such a thing as hydrogen "bond" exists and have ignored the fact that some believe it to be nothing more than an attraction due to dipole interaction. One might evade the argument by simply stating that the association takes place through hydrogen without further implication as to the nature of the interaction. We believe, however, that the evidence warrants a much more detailed picture: The characteristic effect of hydrogen bonding on the fundamental in infrared absorption is the increase in absorption coefficient and the shift of frequency to longer wave length. The increase in absorption coefficient is presumably due to an increase in dipole moment. All of these effects would be accounted for by an increase in the internuclear distance of the hydrogen from its original partner accompanied by a transformation toward the ionic type of bonding. In the case where the hydrogen is not active as in chloroform this transformation is small but in the case of the carboxylic acids the result is the formation of a symmetrical eight-membered ring which can hardly be considered as anything short of a chemical reaction. One may say therefore that all degrees of interaction are to be found but that in general the interaction is more than could be predicted from a simple dipole theory. It must be remembered that the hydrogen bond is formed in non-polar solvents and in the vapor state so that no question of ionization is involved.[12]

One may say, therefore, that the formation of a hydrogen bond involves a definite alteration in molecular structure which is scarcely envisaged in the term dipole interaction; this structure is sufficiently rigid to justify the use of the term bond. The fact that the bond is easily broken does not invalidate the use of the term.

The colligative and other physical properties of the molecule still furnish the best evidence as to the type of association. For example, when dimers are formed the dipole moments tend toward zero while in the case of polymers the polarization is increased. Thus alcohol has a much higher dielectric constant than acetic acid. One may hope, however, that when sufficient data have been obtained on the infrared absorption, vibrational analysis will give a definite picture of the structure in all types of association.

In this paper we shall report the results obtained on the carboxylic acids. Hydrogen bonding between other types of molecules will be discussed in subsequent papers.

Experimental

The infrared spectrograph and other equipment has been described briefly in a previous paper.[8] In the spectrograph a 75-mm. rock salt prism is used with a Littrow mounting. The source of radiation is a 220-volt Nernst glower, and the deflections are read directly from a high sensitivity galvanometer. The resolving power and accuracy of calibration are such as to make all details shown in the accompanying absorption curves significant and reproducible.

In the region in which these results were obtained thin glass proved satisfactory for all windows. The results reported here are mainly for solutions, carbon tetrachloride being the solvent. For absorption in solution the molal absorption coefficient K is calculated, as defined arbitrarily by the expression

$$K = \frac{1}{cd} \log \frac{I_0}{I}$$

Here I is the intensity (as measured by galvanometer deflection) through the solution and I_0 the intensity through an equal thickness of pure solvent; c is the concentration expressed as moles per liter of solution and d is the cell length. Because of insufficient resolving power and other factors

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[12] Scatchard and Raymond [THIS JOURNAL, 60, 1278 (1938)] recently have discussed negative evidence for hydrogen bond formation in chloroform–alcohol solutions. The evidence here is unquestionably that the association of the alcohol is so strong that there is no tendency toward the formation of an intermolecular compound with chloroform. This is because the hydrogen of the alcohol is more active than the hydrogen of the chloroform; *cf.* the article by Zellhoefer, Copley and Marvel referred to above.

K is not independent of the product $c \times d$. In order to make comparisons at different concentrations it is necessary therefore to maintain the product $c \times d$ constant; this was accomplished by using cells of various lengths. When $c \times d$ is maintained constant, the value of K for a static group such as C–H was found to be quite independent of concentration.

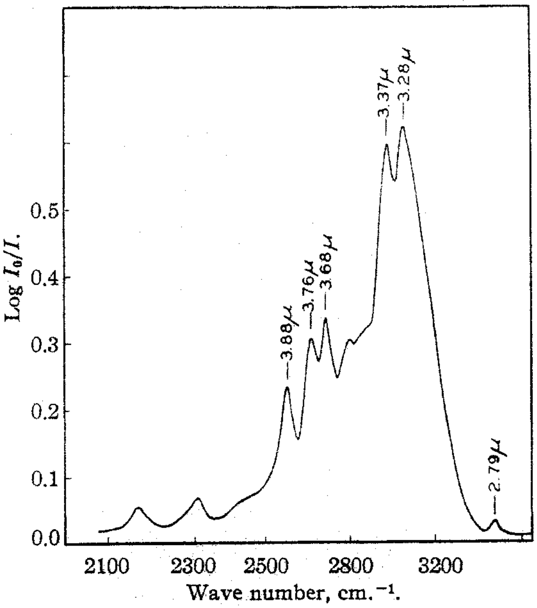

Fig. 1.—Acetic acid vapor: air saturated with acetic acid at 21° in 10.18 cm. cell.

The utmost care was exercised in the preparation and purification of materials, including the solvent material. Benzoic acid was purified by recrystallization from alcohol–water solutions. Acetic acid, benzoyl chloride and trichloroacetic acid were purified by distillation at low pressures.

The deuterobenzoic acid was prepared by heating benzoyl chloride with a fivefold excess of 99.6% deuterium oxide in a sealed tube at 100° for two hours. The deuterium chloride and excess deuterium oxide were removed by distillation at low pressures. The carbon tetrachloride used as solvent was dried over phosphorus pentoxide. After the absorption curve of the deuterated acid was obtained the acid was reconverted to ordinary benzoic acid by exposure to moist air. The absorption curve was identical with ordinary benzoic acid.

The association of acetic acid in the vapor has been recognized for a very long time and many references could be cited to the effect that a dimer is formed. The first direct experimental evidence as to the structure of this dimer was obtained by Pauling and Brockway, as cited above. Electron diffraction does not, however, give information about the hydrogen atoms. Studies have also been made of the Raman spectrum but the method *par excellence* for the observation of the behavior of hydrogen in molecules is infrared spectroscopy.

The infrared absorption spectra of the carboxylic acids have been investigated by a number of workers in recent years, particularly in the vapor. We shall refer here only to work dealing with the absorption due to hydrogen.

Gillette and Daniels[13] observed a complicated spectrum in the region of 3.0 μ which they attributed to C–H and to overtone and combination frequencies. Badger and Bauer[14] have studied the infrared spectrum of acetic acid by photographic methods and have observed what they believe to be shifts in the second overtone frequency which they believe to be due to hydrogen bonding. Davies and Sutherland[15] have studied the effect of temperature on the infrared absorption of solutions of the carboxylic acids. They find that increasing temperature increases the monomeric O–H frequency and report a broad "association" band in trichloroacetic acid at 3.3 μ. Herman and Hofstadter[16] have published a curve showing the infrared absorption of deuteroacetic acid, CH_3COOD, and have suggested that the absorption band at 4.3 μ is due to deuterium bonding. Only a very weak C–H absorption was observed.

In the accompanying curves are shown the infrared absorption in the region of the C–H and O–H fundamental for acetic acid, trichloroacetic acid, benzoic acid and deuterobenzoic acid. One curve is shown for acetic acid vapor. Comparison with the curve for acetic acid in carbon tetrachloride solution shows that the absorption is the same in solution except that there is a shift of 0.01–0.02 μ toward longer wave lengths in solution. We may therefore assume that any conclusions drawn from our observations in solution apply to the vapor of acetic acid.

An examination of the curves in Fig. 2 shows that acetic acid is slightly dissociated into single

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(13) R. H. Gillette and F. Daniels, This Journal, **58**, 1139 (1396); R. H. Gillette, *ibid.*, **58**, 1143 (1936).

(14) R. M. Badger and S. H. Bauer, *J. Chem. Phys.*, **5**, 369, 605, 839, 852 (1937).

(15) M. M. Davies, G. B. and B. M. Sutherland, *Nature*, **141**, 372 (1938).

(16) R. C. Herman and R. Hofstadter, *J. Chem. Phys.*, **6**, 110 (1938).

molecules at 0.0005 *M* solution; much less so in 0.008 *M* solution. The unbounded hydroxyl band is at 2.82 μ; the slight absorption at 2.67 μ being due to water. A study of Figs. 3 and 4 shows that the absorption due to C–H must be very slight. This is a point about which Daniels and Gillette were uncertain but it is clear that both benzoyl chloride and deuterobenzoic acid have very little absorption in this region and some of the absorption in the case of the deuterobenzoic acid is undoubtedly due to the presence of a small amount (~1%) of ordinary benzoic acid. It will be further noted that the absorption of trichloroacetic is very similar to that for acetic and benzoic acids.

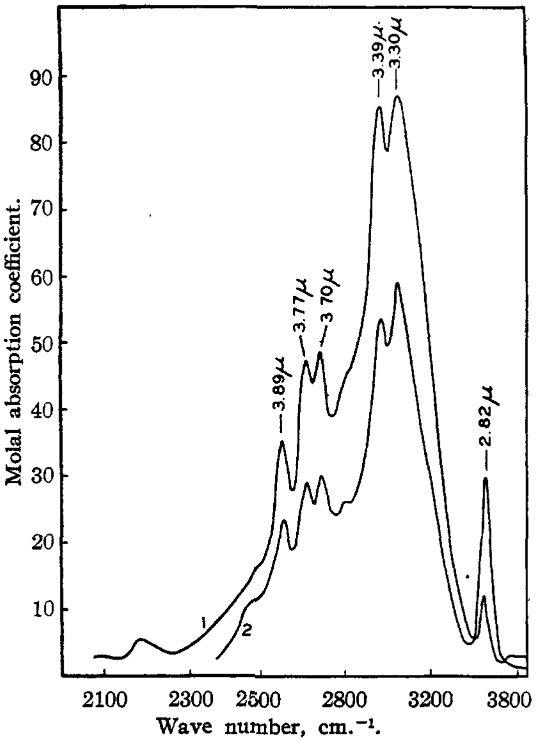

Fig. 2.—Acetic acid: (1) 0.008 *M* in 0.640 cm. cell; (2) 0.0005 *M* in 10.18 cm. cell.

One may therefore conclude that the strong absorption in the neighborhood of 3.3 μ is due mainly to the hydrogen bonding as Herman and Hofstadter suggest. In deuterobenzoic acid the absorption band is narrower and apparently simpler in structure, although the shift in the principal peak is just what one would calculate for deuterium substitution.

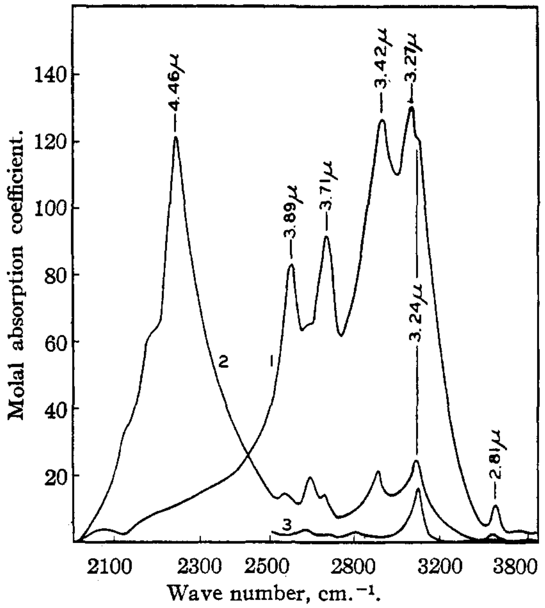

Fig. 3.—(1) Benzoic acid, 0.008 M solution in 0.640 cm. cell; (2) deuterobenzoic acid, 0.008 *M* solution in 0.640 cm. cell; (3) benzoyl chloride, 0.008 *M* solution in 0.640 cm. cell.

It is evident that the absorption band for the acids contains two or more pairs of doublets. The exact identification of these doublets must await the vibrational analysis of the carboxylic dimer. This has been undertaken by Dr. F. T. Wall of this Laboratory. Meanwhile one may speculate as to the probable cause of the doublet

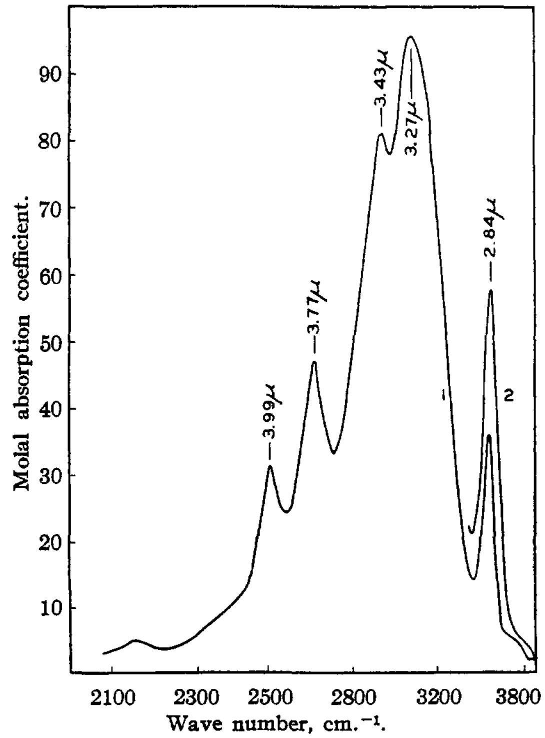

Fig. 4.—Trichloroacetic acid: (1) 0.008 *M* in 0.640 cm. cell; (2) 0.0005 *M* in 10.18 cm. cell.

structure observed. If we assume that the hydrogen atoms are placed unsymmetrically in the eight-membered ring formed by the two carboxyl groups, *i. e.*, each hydrogen being nearer to the oxygen to which it was originally attached, then there are two modes of vibration involving the stretching of the hydrogen bonds which are active in infrared absorption. Each vibration is antisymmetric with respect to a center of symmetry but they differ in the relative motions of the oxygen atoms on either side of the hydrogen atoms. These two frequencies might be guessed to differ by the separation of the two pairs of doublets, *viz.*, 50 cm.$^{-1}$. Because of the fact that there are alternative positions for each hydrogen and consequently, a double minimum in the potential energy curve, the doublets themselves might be expected. Their separation varies from 10 to 20 cm.$^{-1}$. This is, of course, to say nothing of the possibility of resonance between the O–H and C–H vibrations which have nearly the same frequency. Since the C–H absorption is small this effect is probably unimportant although the C–H absorption might be considerably increased by the resonance itself.[17]

Some plausibility is lent to the foregoing explanations by the much simpler structure observed in the absorption peak for deuterobenzoic acid. Here the last effect is absent and because of the greater mass of the deuterium atom the doublet separation would be too small for resolution. There would remain only the two modes of vibration differing markedly in absorption coefficients and these appear to be present.

It has been noted by various authors that formic acid in the liquid state has a dielectric constant some ten times that of liquid acetic acid. Because of the difficulty of purification no studies have been made upon formic acid but there can be little doubt that in the liquid state the dimers are transformed into higher polymers perhaps through the hydrogen attached to the carbon. In a subsequent paper this possibility will be discussed again in connection with formamide. The high dielectric constant which results from polymerization such as occurs in formamide probably offers a clue to the explanation of the greatly reduced solubility of chloroform in this solvent.

The authors wish to acknowledge their indebtedness to the Rockefeller Foundation for funds which enabled them to conduct this research.

Summary

The general character of the infrared absorption spectra indicative of hydrogen bonding is discussed. Curves are shown for the absorption of the active or bonding hydrogen in acetic, benzoic and deuterobenzoic acids under various conditions. The generalization of Venkateswaran in regard to the shift of the hydroxyl frequency is confirmed and some suggestions are made to explain the complex absorption characteristic of association in the carboxylic acids.

URBANA, ILLINOIS RECEIVED JUNE 30, 1938

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[17] In a previous note [THIS JOURNAL, 59, 176 (1937)] the authors reported on the lack of evidence for the enolization of dibenzoylmethane. This molecule shows absorption resembling that of the carboxylic acids and it is possible to write a hydrogen bonded structure for the enolic form that resembles one-half of the dimeric ring of the acids. The matter therefore requires further investigation.

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Negative Temperature Coefficient in the Rate of Propane Oxidation

BY ROBERT N. PEASE

In the early work[1] on the slow combustion of propane and the butanes, it was noted that under certain conditions the rate of oxidation decreased markedly with increasing temperature, although eventually (at a higher temperature) explosion occurred. Similar observations have since been made by Beatty and Edgar[2] on heptane–air mixtures, by Aivazov and Neumann[3] on pentane–oxygen mixtures, and by Newitt[4] on propane–oxygen mixtures.

The beginnings of an explanation of this anomalous behavior follow from the latter investigation. It had been found by Townend[5] that mixtures of air with vapors of hydrocarbons, alcohols, or aldehydes show, in addition to a "true ignition" region (higher pressures and temperatures), a region of limited explosibility giving rise to so-

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[1] Pease, THIS JOURNAL, **51**, 1839 (1929).

[2] Beatty and Edgar, *ibid.*, **56**, 102 (1934).

[3] Aivazov and Neumann, *Acta Physicochimica* (U. R. S. S.), **4**, 575 (1936).

[4] Newitt, *et al.*, *J. Chem. Soc.*, 1656, 1665, 1669 (1937).

[5] Townend, *Chem. Rev.*, **21**, 259 (1937).