spectively, being used. The same catalyst was used throughout, as it could be filtered and dried at 100° after each experiment without impairing its activity.

Summary

The hydrogenation of various quinones in a hydrogen atmosphere in the presence of palladium catalysts produces hydroquinone with great speed, provided mineral acids are absent. The same reaction takes place with platinum charcoal, but more slowly. Platinum charcoal is active even in the presence of mineral acid, hydroquinone being only the first stage of the reaction which has cyclohexanol as the final product.

NEWARK, N. J. RECEIVED FEBRUARY 12, 1940

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

The Kinetics of Neutralization

BY MARTIN KILPATRICK

In a recent paper Lewis and Seaborg[1] have reported the study of the rate of fading of the blue trinitrotriphenylmethide ion in acid solutions. They interpret their results in terms of their classification of acids and bases as primary and secondary.[2,3]

Another kinetic interpretation of their results merits consideration. Considering the reaction to be catalyzed by acids we may write

$$\mathrm{B_{S}}\text{-} \underset{k_{-1}\mathrm{A^-}}{\overset{k_1\,\mathrm{HA}}{\rightleftarrows}} \mathrm{B_{P}}\text{-} \qquad (1)$$

where $\mathrm{B_S}$- represents the blue ion, called the secondary base by Lewis, $\mathrm{B_P}$- the form called the primary base, HA any acid, and $\mathrm{A^-}$ its conjugate base. This reaction is followed by the reaction

$$\mathrm{B_{P}}\text{-} + \mathrm{HA} \overset{k_2}{\rightleftarrows} \mathrm{HB} + \mathrm{A^-} \qquad (2)$$

In other words, equation (1) is step (a) in the paper of Lewis and Seaborg (who do not, however, consider the acid–base catalytic nature of the reaction) and equation (2) represents the second step. In equation (1) $\mathrm{B_S}$- is transformed to $\mathrm{B_P}$- by the catalyst HA, the reverse process being catalyzed by the base $\mathrm{A^-}$. Now if the reaction $\mathrm{B_P}$- + HA is much faster than the reaction $\mathrm{B_S}\text{-} \rightarrow \mathrm{B_P}\text{-}$, and if $k_2C_{\mathrm{HA}} \gg k_{-1}C_{\mathrm{A}^-}$, the rate equation would be

$$-\frac{\mathrm{d}C_{\mathrm{B_S}\text{-}}}{\mathrm{d}t} = k_1C_{\mathrm{B_S}\text{-}}C_{\mathrm{HA}} \qquad (3)$$

and the reaction would be of the second order in agreement with the experimental findings of Lewis and Seaborg. Lewis and Seaborg consider that a small concentration of $\mathrm{B_P}$- is maintained in equilibrium with $\mathrm{B_S}$- and that the rate-determining step is the reaction of the primary base $\mathrm{B_P}$- with the acid HA. They conclude that ". . . 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." In the present paper it is assumed that the change from $\mathrm{B_S}$- to $\mathrm{B_P}$- requires an acid catalyst and that $\mathrm{B_P}$- reacts rapidly with the acid if it is sufficiently strong.

The measured energies of activation for the stronger acids are found to average 9.1 kcal., and the energy of activation is calculated to be 8.9 for alcohol. The constancy of this value is not in contradiction to a catalytic mechanism. For example, in the mutarotation of glucose the measured energies of activation for such different catalysts as water, pyridine, acetate ion, and hydrogen ion were found to be 17.6, 19.1, 18.0, and 19.3 kcal., respectively.[4] In the enolization of acetoacetic ester[5] and in the iodination of acetone[6] the measured energies of activation for different catalysts are practically the same. From the data it is evident that the statement of Lewis and Seaborg "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" is hardly in accord with the facts for reactions showing general acid and basic catalysis.

Turning now to the alcohol reaction, Lewis and Seaborg state "Alcohol is itself an acid, and although its acid strength is not high

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[1] Lewis and Seaborg, THIS JOURNAL, **61**, 1894 (1939).

[2] Lewis, *J. Franklin Inst.*, **226**, 293 (1938).

[3] Lewis and Seaborg, THIS JOURNAL, **61**, 1886 (1939).

[4] Kilpatrick and Kilpatrick, *Ibid.*, **53**, 3698 (1931).

[5] Pedersen, *J. Phys. Chem.*, **38**, 601 (1934).

[6] Smith, *J. Chem. Soc.*, 1774 (1934).

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 stronger acids, 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...." The reaction scheme therefore includes a reaction of the primary base with alcohol. In the new interpretation the blue form is already in equilibrium with B_P-, and as soon as the acid is added the species B_P- is removed and the change of B_S- to B_P- is catalyzed by two acids, the acid added, which is present in small concentration, and the acid alcohol. That is

$$-dC_{B_S^-}/dt = k'C_{B_S^-}C_{C_2H_5OH} + k''C_{B_S^-}C_{HA} \quad (4)$$

The molar catalytic constant k'' will be greater than k' because of the greater strength of the acid but the "preponderating" part played by the alcohol is due to its high concentration. In addition, since the concentration of alcohol is constant, the observed velocity constant should no longer be truly of the second order for the weaker acids, and this is in agreement with the experimental results. If the greater part of the reaction is by way of the alcohol, the last term in (4) becomes unimportant, and the rate of reaction will no longer be sensitive to change in concentration of the acid HA. This is also in accord with the experimental results.

The velocity constants range from 30 for the strongest acid (monochloroacetic acid) to 0.09 for phenol, and this difference in velocity is explained by the statement "It appears as though increasing polarization of the acid, by its orienting effect, increases the probability that a given collision between the acid and primary base will be effective." In terms of the catalytic mechanism a different velocity constant for each catalyst is expected. From the concentration of B_P- in equilibrium with B_S-, and from the velocity constant for the reaction between the blue ion and chloroacetic acid, Lewis and Seaborg compute that the molar velocity constant for the reaction between the primary base and chloroacetic acid is 6×10^{10}, time being expressed in seconds. This would mean that there was a high probability of reaction at each collision. Lewis regards this calculation as erroneous. Now the experimental results for chloroacetic acid can be expressed by an equation of the Arrhenius type

$$\ln k = 27.5 - 10{,}200/RT \quad (5)$$

and the value 27.5 is in reasonable agreement with other acid–base catalyzed reactions. The corresponding values for the other catalysts range from 25.5 to 21.5. If the collision number were 10^{11} the value would be approximately 25.

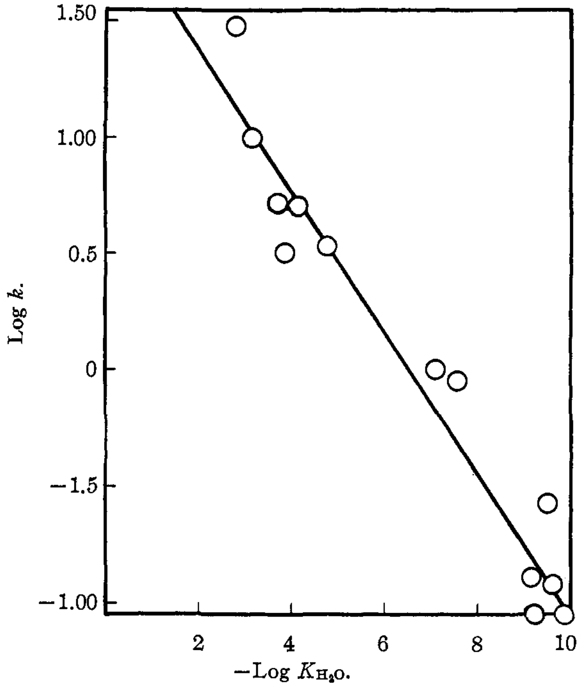

Fig. 1.

The characteristic of all reactions showing general acid catalysis is the relation between the catalytic constant (k) and the acid strength constant (K)

$$k = GK^x \quad (6)$$

where G and x are constants for a series of catalysts of similar structure and charge type. For acids of different structure the relation is an approximate one. The following graph indicates that the relationship holds approximately in the present case. Lewis considers this relationship to be erroneous.[7] It should be pointed out that the velocity constants given in Table I of the paper by Lewis and Seaborg, and plotted here, include the alcohol reaction, so that the catalytic constants assigned to the weaker acids are somewhat too high.

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(7) Lewis, *J. Franklin Inst.*, **226**, 293 (1938).

Summary

The neutralization of trinitrotriphenylmethide ion is interpreted as an acid-catalyzed reaction. The interpretation is in accord with the kinetic experiments.

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[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY]

Thermodynamic Properties of the Hexyl Alcohols. IV. 3-Methylpentanol-1 and 2-Methylpentanol-5

BY FRANK HOVORKA, HERMAN P. LANKELMA AND ISADORE SCHNEIDER[1]

This paper represents the fourth[2,3,4] of a series of investigations being carried out in this Laboratory concerned with the relation between physical properties and chemical constitution of the hexyl alcohols, and deals with the preparation, purification and determination of the vapor pressure, viscosity, density, surface tension and refractive index of 3-methylpentanol-1 and 2-methylpentanol-5 (4-methylpentanol-1).

Experimental

Preparation of Materials.—Both alcohols were prepared in a manner similar to that described by Dreger[5] for the preparation of hexanol-1. 3-Methylpentanol-1 was made by the Grignard reaction using secondary butyl bromide and ethylene oxide. Similarly, 2-methylpentanol-5 was prepared from isobutyl bromide and ethylene oxide.

Purification.—The alcohols were allowed to stand over "Drierite"[6] for a period of two months, filtered from the drying agent and fractionally distilled. The fractionating columns used have been described previously.[3]

The alcohols were considered pure when the boiling point range did not exceed 0.02°.

Apparatus.—A complete description of the apparatus and technique used for the determination of the physical constants can be found in the paper by Hovorka, Lankelma and Stanford.[3]

All the instruments used in the surface tension, density, and viscosity measurements were recalibrated before determinations were made.

Discussion of Results

Vapor Pressure.—The vapor pressure data are tabulated in Table I, column 5.

The summary of the values calculated from the vapor pressure data is given in Table II. The temperature variation of the vapor pressure was found to be given very closely by the Rankine equation, whose constants *A*, *B* and *C* are listed.

The values of the Trouton constant are considerably higher than the normal value of 21. These high values correspond with those found for the hexanols previously reported.[2,3,4]

Viscosity.—The viscosity data are tabulated in Table I, column 3. The viscosity *vs.* temperature curves for the two hexanols cross at 65° although the values from 65–150° do not vary by more than 0.6%. This peculiar behavior has been noticed previously. Like hexanol-1, reported by Hovorka, *et al.*, these two alcohols have a small temperature coefficient of viscosity.

Plots of Raman's equation[7] and Andrade's equation[8] yielded perfectly symmetrical curves instead of the required straight lines. The constants of the two equations and the deviations of the calculated from the observed viscosities are listed in Table III. It is very interesting to note here that of all the hexyl alcohols so far studied, hexanol-1 gives the least deviation from Andrade's equation, and that it is closely followed by 2-methylpentanol-5 and 3-methylpentanol-1.

Values of the degree of association have been calculated from the fluidity using a formula proposed by Bingham, *et al.*[9,10] The association factor as determined by the fluidity method is the ratio of the temperature required to give a certain fluidity to the temperature calculated from the "atomic temperature" constants. The values obtained are listed in Table IV. Calculation of the association factor for hexanol-1 gave values of 1.59, 1.48 and 1.41.

Bingham further calculates the degree of association by application of the formula, n =

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[1] Abstracted from a Thesis by I. Schneider, submitted to the Graduate School of Western Reserve University, in partial fulfillment of the requirements for the Degree of Master of Arts, May, 1937.

[2] Hovorka, Lankelma and Naujoks, THIS JOURNAL, **55**, 4820 (1933).

[3] Hovorka, Lankelma and Stanford, *ibid.*, **60**, 820 (1938).

[4] Hovorka, Lankelma and Axelrod, *ibid.*, **62**, 187 (1940).

[5] "Organic Syntheses," Coll. Vol. 1, p. 299.

[6] Hammond and Withrow, *Ind. Eng. Chem.*, **25**, 1112 (1933).

[7] Raman, *Nature*, **111**, 532 (1923).

[8] Andrade, *Phil. Mag.*, **17**, 698 (1934).

[9] Bingham and Darrall, *J. Rheol.*, **1-2**, 174 (1929-31).

[10] Bingham and Spooner, *ibid.*, **3**, 228 (1932).