4. The data lead to the conclusion that the slow process of adsorption may be described as an interaction between molecules adsorbed by van der Waals forces and surface atoms which receive the necessary activation energy.

5. Such a process is in accord with previous observations on the velocities of adsorption of hydrogen and deuterium at atmospheric pressure on chromic oxide gel in the same temperature range.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

A Kinetic Correlation of Two Reactions Involving Hydrogen Peroxide. Its Oxidations by "Chloramine T" and by Chlorine

BY HERMAN A. LIEBHAFSKY

Although the use of "chloramine T," TSO_2NClNa,[1] as an analytical reagent is no longer new,[2] the kinetics of reactions involving this interesting oxidizing agent (or similar nitrogen compounds) have not been extensively investigated. Coull, Hope and Gouguell[3] have recently measured the rate at which hydrogen peroxide is oxidized in 0.15 *M* hydrochloric acid solutions containing "chloramine T" at concentrations near 0.006 *M*. They conclude that chlorine reacts directly with the peroxide and that "it becomes necessary. . .to designate the 'chloramine T' entering the reaction as 'active'." We shall show that a satisfactory mechanism for the stoichiometric reaction

$$TSO_2NHCl + H_2O_2 = TSO_2NH_2 + H^+ + Cl^- + O_2 \quad (1)$$

can be formulated without their assumption of an "active" species, and that their results agree with those of Makower and Bray[4] for the reaction

$$Cl_2 + H_2O_2 = 2H^+ + 2Cl^- + O_2 \quad (2)$$

When TSO_2NClNa is dissolved in water, the hydrolysis equilibrium

$$TSO_2NCl^- + H_2O \rightleftarrows TSO_2NHCl + OH^- \quad (3)$$

will be rapidly established; presumably TSO_2ClH is a weak acid, so that we may expect a small, but appreciable, fraction of its anion to be hydrolyzed. When such a solution is acidified, the stoichiometric reaction

$$TSO_2NCl^- + H^+ = TSO_2NHCl \quad (4)$$

occurs. The chemistry of TSO_2NHCl and similar compounds is consistent with the assumption that these substances in aqueous solution are in rapid equilibrium with hypochlorous acid and, if hydrochloric acid is present, with chlorine; thus

$$TSO_2NHCl + H_2O \rightleftarrows TSO_2NH_2 + HClO \quad (5a)$$

$$TSO_2NHCl + H^+ + Cl^- \overset{K_5}{\rightleftarrows} TSO_2NH_2 + Cl_2 \quad (5)$$

Since the hydrolysis equilibrium of chlorine

$$Cl_2 + HO_2 \overset{K_6}{\rightleftarrows} HClO + H^+ + Cl^- \quad (6)$$

is always maintained in an aqueous hydrochloric acid solution, Equilibria 5a and 5 are alternative ways of describing the experimental fact that an acid TSO_2NClNa solution contains "free" chlorine ($HClO$ or Cl_2) in equilibrium amount.

The experimental results of Coull, Hope and Gouguell will now be interpreted by assuming that Equilibria 5a, 5 and 6 are always maintained in reaction mixtures prepared by adding hydrochloric acid to aqueous solutions of TSO_2NClNa and H_2O_2, and that the rate of Reaction 1 is equal to the rate at which Reaction 2 proceeds. In dilute hydrochloric acid solution the rate of Reaction 2 (specific rate, χ_2) is given by

$$-d(H_2O_2)/dt = \chi_2 \frac{(Cl_2)}{(H^+)(Cl^-)(\gamma_\pm)^2}(H_2O_2) \quad (2a)$$

With Equilibrium 5 maintained

$$(Cl_2) \doteq K_5(TSO_2NHCl)\ (H^+)\ (Cl^-)\ (\gamma_\pm)^2/(TSO_2NH_2)$$

therefore

$$-d(H_2O_2)/dt =$$

$$\chi_2 K_5 \frac{(TSO_2NHCl)}{(TSO_2NH_2)}(H_2O_2) = k\frac{(TSO_2NHCl)}{(TSO_2NH_2)}(H_2O_2) \quad (1a)$$

The simple expression on the right, to which our rate law leads, becomes identical with that employed by Coull, Hope and Gouguell to explain the rate law of Reaction 1 if we grant that (TSO_2NHCl) is roughly 90% that formed from the "chloramine T" initially added. They assumed that this 90% is "active," but an active species does not usually constitute so large a proportion

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(1) "T" in the formula of a compound will represent the *p*-toluyl radical. For the other abbreviations and conventions, see ref. 5, p. 90.

(2) (a) Noll, *Chem. Zeit.*, **48**, 845 (1924); *cf.* (b) Komarowsky, Filonowa and Korenman, *Z. anal. Chem.*, **96**, 321 (1934).

(3) Coull. Hope and Gouguell, THIS JOURNAL, **57**, 1489 (1935).

(4) (a) Makower and Bray, *ibid.*, **55**, 4765 (1933); (b) Makower, *ibid.*, **56**, 1315 (1934).

of a reacting substance. We shall assume that this 90% represents *all* the TSO_2NHCl present, the other 10% (denoted by Δ) having disappeared to form Cl_2, $HClO$ (Reactions 5 and 5a), and TSO_2NH_2; also TSO_2NCl_2 if the equilibrium

$$2TSO_2NHCl \xrightleftharpoons{K_7} TSO_2NH_2 + TSO_2NCl_2 \qquad (7)$$

has to be considered. Now

$$\Delta = (Cl_2) + (HClO) + 2(TSO_2NCl_2) \qquad (8)$$

is to be identified[3] with b-N; since TSO_2NH_2 is formed in Reaction 1, Δ will decrease as the reaction progresses; b-N should therefore be only an average value of Δ.

We have now shown that our mechanism for Reaction 1 is highly plausible because it yields a rate law that is formally correct. This mechanism (*i. e.*, Equilibria 5, 5a and 6 established, followed by Reaction 2) is quantitatively verified when it has been shown that the rate of Reaction 1 is actually the rate at which Reaction 2 would proceed in the same reaction mixture at the same (HCl) and (Cl_2). (Cl_2) is unknown, but we may assume provisionally that $(Cl_2) = (TSO_2NH_2) = \Delta = 0.1\ (TSO_2NHCl)$ *initially*. By equating the right-hand members of Equations 1a and 2a, and substituting, we obtain

$$\chi_2\,[0.1(TSO_2NHCl)/(H^+)(Cl^-)(\gamma_\pm)^2] = 10\,k \qquad (9)$$

For (HCl) = 0.15 and $(TSO_2NHCl) = 6(10^{-3})$, Coull, Hope and Gouguell found $k = 0.016$; Equation 9 shows the corresponding value of χ_2 to be near 5, which is to be compared with the experimental values derived from a study of Reaction 2. Makower and Bray found that these experimental values decrease precipitously as (HCl) is decreased below 2*M;* at (HCl) = 0.38, the lowest concentration they investigated, $\chi_2 = 850$. No accurate extrapolation to (HCl) = 0.15 can be made, but $\chi_2 \leqslant 80$ is a fair guess; Reaction 1 thus gives a value of χ_2 about one-sixteenth that given more directly by Reaction 2. This sixteen-fold discrepancy is by no means fatal, for (1) the extrapolation of Makower and Bray's data is extremely uncertain, (2) Δ^2 enters into the calculation, (3) (Cl_2) will be appreciably less than Δ if Reaction 7 has to be considered. On the other hand, $\Delta = 0.1$ is not based on initial rate measurements, which should yield a higher Δ and hence a lower χ_2.

It seems fair to say that our mechanism for Reaction 1 is highly probable, and the correlation of Reactions 1 and 2 well established. This mechanism explains why the oxidation of hydrogen peroxide by "chloramine T" does not proceed until the reaction mixture is acidified,[3] for it indicates that TSO_2Cl^-, unlike TSO_2NHCl, is not in equilibrium with an appreciable concentration of chlorine (*cf.* Reactions 3 and 5). It is capable of verification by experiments which cannot be discussed in detail—such work should include the measurement of initial rates, with and without added TSO_2NH_2, perhaps by following oxygen evolution; the dependence of the rate on (H^+) and on (Cl^-); and the correlation of the specific rate constants thus obtained with the equilibrium constants K_5, K_6 and K_7, independently determined.

If Reactions 1 and 2 are related in the manner assumed above, then kinetic study of the former should be a powerful tool for investigating Reaction 2, which is unusually interesting because it alone is anomalous in the halide–halogen–hydrogen peroxide family of reactions. The simplest interpretation of Equation 2a assumes

$$HClO + H_2O_2 \longrightarrow H_2O + H^+ + Cl^- + O_2 \quad (8)$$

to be the only rate-determining step for Reaction 2; that such cannot be the case is shown by these experimental facts: (1) Reaction 2 obeys the Arrhenius law[4a,5] and (2) hypochlorous acid when mixed with hydrogen peroxide without adding hydrochloric acid reacts at about one-millionth the rate to be expected from experimental results in strongly acid solutions.[4a] Heretofore, the only experimental method for measuring the rate of Reaction 2 at low (HCl) has been a flow method[4a] that yields only one point in each experiment and has not been used below (HCl) = 0.38 because the reaction is too rapid at these low concentrations. The evaluation of χ_2 from rate measurements on Reaction 1 seems to involve no such difficulties; it should be possible in this way to study Reaction 2 in an important concentration region hitherto inaccessible.

Summary

The oxidation of hydrogen peroxide by "chloramine T" has been assigned a plausible mechanism which conforms with its rate law, and which correlates it with the reaction between hydrogen peroxide and chlorine. The experimental evidence now available for both reactions lends approximately quantitative support to this mecha-

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(5) Liebhafsky [*Chem. Rev.*, **17**, 89 (1935)] has shown that reactions whose rate-determining step involves HXO or XO^- should not obey the Arrhenius law.

nism, but further work is necessary for complete proof. If this mechanism is correct, the "chloramine T" reaction furnishes a way of studying the anomalous chlorine–peroxide reaction in a concentration region hitherto inaccessible.

SCHENECTADY, NEW YORK RECEIVED FEBRUARY 15, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE WASHINGTON SQUARE COLLEGE OF NEW YORK UNIVERSITY]

Thiazolinephenols.[1,2] Their Synthesis and Structure Proof

BY JOSEPH B. NIEDERL, WILLIAM F. HART AND JOHN V. SCUDI

Theoretical Part

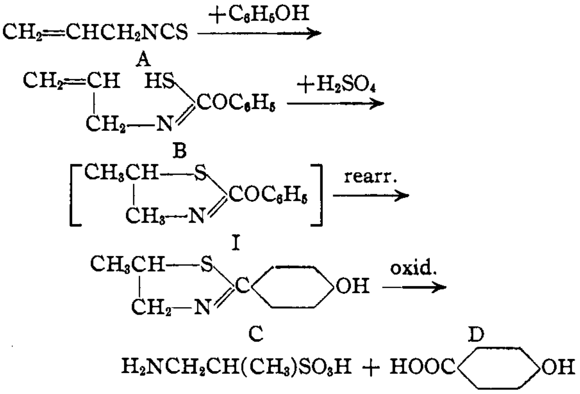
In the course of systematic investigations of the condensations of phenols with unsaturated compounds containing nitrogen (unsaturated amines, ureas, cyanides, isocyanides, isocyanates, thiocyanates and isothiocyanates)[3] the condensation system "phenols–allyl mustard oil" is of particular interest, because instead of straight addition of the phenol to the ethylenic linkage, the formation of thiazolinephenols took place, as set forth in this communication.

Since thiazolinephenols do not appear to be reported in the literature, investigation of the reaction mechanism as well as structure proof of the condensation products was necessary. By analogy of the reported rearrangement of allyl thiourea, aryl thioureas, allylthiocarbaminyl semicarbazide and thiosemicarbazide[4] to the corresponding thiazolines under the influence of cationoid reagents, the formation of thiazolinephenol from allyl mustard oil, phenol and concentrated sulfuric acid, can then be explained best by a similar reaction mechanism.

The observed and normal formation of the allylphenyl thiourethan (A)[5] from allyl isothiocyanate and phenol must be taken in account first, followed by cyclization under the influence of the acidic condensing agent to the 5-methyl-2-phenoxythiazoline (B). The required subsequent rearrangement of this non-isolated intermediary ether to the final 5-methyl-2-(4′-hydroxy)-phenylthiazoline (I), in presence of sulfuric acid, can be regarded as being analogous to the rearrangement of secondary alkyl phenyl ethers already known.[6]

To prove the structure more fully, the above thiazolinephenol was oxidized, employing the method of Andreasch, Prager and others[4a,b,7] and β-methyltaurin (C), together with *p*-hydroxybenzoic acid (D), were isolated.

Graphically, the reaction mechanism as well as the structure proof may then be presented as follows.



To illustrate that the above scheme represents a fairly general reaction, not only phenol (I, Ia, Ib) itself was condensed with mustard oil, but also its alkylated homologs (*m*-cresol II, IIa, IIb) and related dihydroxy compounds (guaiacol III, IIIa, IIIb and resorcinol IV, IVa, IVb), all yielding the corresponding thiazolinephenols, as enumerated in the table given.

Experimental Part

Condensation Method.—To a mixture consisting of 0.5 mol of allyl mustard oil and one mol of phenol, cooled to 0–5°, one mol of concd. sulfuric acid, kept at the same temperature, was slowly added under constant stirring or agitation. The same low temperature was maintained not only throughout the entire addition of the condensing agent, but also for the next twenty-four hours, after which

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[1] Presented at the Kansas City meeting of the American Chemical Society, April, 1936.

[2] From Part I of the thesis presented by William F. Hart to the Faculty of the Graduate School of New York University in candidacy for the degree of Doctor of Philosophy.

[3] Niederl and co-workers, THIS JOURNAL, **53**, 277 (1931); **55**, 2571 (1933); **56**, 2412 (1934).

[4] (a) S. Gabriel, *Ber.*, **22**, 2984 (1889); (b) B. Prager, *ibid.*, **22**, 2991 (1889); (c) J. Gadamer, *Arch. Pharm.*, **234**, 20 (1896); (d) H. Will, *Ann.*, **52**, 11 (1844); (e) Busch and Lotz, *J. prakt. Chem.*, [2] **90**, 270 (1914).

[5] Schneider and Wrede, *Ber.*, **47**, 2042 (1914).

[6] Niederl and co-workers, THIS JOURNAL, **53**, 1928 (1931); **54**, 1063 (1932); **55**, 284 (1933); Sprung and Wallis, *ibid.*, **56**, 1715 (1934); Sowa, Hinton and Nieuwland, *ibid.*, **55**, 3402 (1933); **54**, 2019 (1932); R. A. Smith, *ibid.*, **56**, 717 (1934).

[7] Andreasch, *Monatsh.*, **4**, 134 (1883); Young and Crookes, *J. Chem. Soc.*, **89**, 71 (1896).