appreciable heat of activation, it appears that the destruction of acetanilide follows such a scheme as acnd + OH → X, X + OH → Y, in which X is a free radical which is not sufficiently reactive to propagate the decomposition chain but yet an effective inhibitor and Y is a stable oxidation product of acetanilide. The removal of effective inhibitor then requires two chain-carrying radicals and hence depends twice on the heat of activation of the chain-initiating process. Since there is, no doubt, an inverse relationship between the acetanilide concentration and the steady state active radical concentration, this mechanism involving two radicals predicts an apparent negative order for the destruction of inhibitor, in agreement with the results in Table I showing the induction period more than proportional to the initial acetanilide concentration.

The strong piece of evidence presented by Haber and Weiss for their chain mechanism for the reaction is the extremely rapid disappearance of hydrogen peroxide during the oxidation of ferrous ion to ferric by the peroxide. Under certain conditions they were able to show the disappearance of hydrogen peroxide during this short interval to be several times that needed to oxidize the ferrous. In order to test the relationship between the effect of ferrous ion and the effect of acetanilide on hydrogen peroxide decomposition a number of experiments were run under the conditions of expt. 8 in Table I, except that a portion of the iron present in the solution at the start of the reaction was ferrous. Results of these experiments are given in Table II. It can be seen that ferrous ion decreases markedly the induction period, since the addition of ferrous ion to hydrogen peroxide solutions produces a large number of free radicals in a short time and hence causes considerable inhibitor destruction during that period. The third column in Table II gives the decrease in concentration of acetanilide during the oxidation of ferrous calculated under the assumptions that the induction period is due to the remaining acetanilide and the relationship between induction period and acetanilide concentration is that shown in Table I.

TABLE II

EFFECT OF FERROUS ION

Initial (Fe^{++})	Induction, min.	$10^4 \times$ acnd loss[a]	Mean cons. ratio	H_2O_2 loss[a]	H_2O_2 loss / acnd loss
0.0000	55	0.00	..	0.0000	..
0.0073	26	2.3	1.27	0.0056	24
.015	14	3.4	1.08	.0089	26
.022	5	4.3	1.0	.0112	26
.029	4.5	4.5	0.89	.0112	25
.036	3[b]	4.7	0.81	.011	23
.015	0	[c]	1.14	.0098	..

[a] In moles/l. [b] Too short for good estimate. [c] Experiment with no acetanilide.

Although hydrogen peroxide is catalytically decomposed by the ferric ion after the ferrous has been oxidized, the rate is sufficiently slow, especially in the presence of acetanilide, that the peroxide concentration immediately after the ferrous oxidation can be extrapolated quite accurately. With an analysis of the peroxide stock solution, it is then possible to calculate the Haber and Weiss "mean consumption ratios," $\Delta H_2O_2/\Delta Fe^{++}$, as shown in column 4 of Table II; this quantity is 0.5 if the peroxide consumption is equivalent to the ferrous ion oxidized. It might be remarked that the equation developed by Abel neglecting the possibility of a chain reaction predicts a much smaller mean consumption ratio under the conditions of these experiments. It is of interest to compute in addition the hydrogen peroxide *decomposed*, that is, disappeared in excess of that needed to oxidize the ferrous ion; this is given in column 5, the ratio of this quantity to the acetanilide loss in column 6. From the proportionality of the peroxide and acetanilide losses it appears that the destruction of each depends in the same way on the concentrations of the other substances. Since the decomposition of peroxide is a sequence of two radical reactions, this is consistent with the mechanism of inhibitor destruction proposed on the basis of the experiments without ferrous ion. Since the peroxide loss is about 25 times the acetanilide loss, the specific rate of the acetanilide reaction is only about 4 times that of the peroxide decomposition; this is insufficient to explain the marked decrease in peroxide decomposition rate due to acetanilide without a chain mechanism.

The effect described here is exactly that expected of an inhibitor of a typical chain reaction and hence we are led to the conclusion that the ferric catalyzed hydrogen peroxide decomposition is a chain reaction as proposed by Haber and Weiss. The action of acetanilide appears to be the removal to two chain-carrying radicals by each acetanilide molecule.

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1-Pentenyl-1-trichlorosilane

BY CHARLES A. BURKHARD

In a previous paper[1] the reaction of acetylene and trichlorosilane in the presence of peroxide giving 1,2-bistrichlorosilylethane was described. A two-step reaction was postulated.

$$RC{\equiv}CH + HSiCl_3 \xrightarrow{\text{Peroxide}} RCH{=}CHSiCl_3 \quad (1)$$

$$RCH{=}CHSiCl_3 + HSiCl_3 \xrightarrow{\text{Peroxide}} Cl_3SiRCHCH_2SiCl_3 \quad (2)$$

The first step involves the addition of one molecule of trichlorosilane to acetylene to give vinyl-

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[1] Burkhard and Krieble, THIS JOURNAL, 69, 2687 (1947).

trichlorosilane while the second step involves the addition of a molecule of trichlorosilane to vinyltrichlorosilane to give 1,2-bistrichlorosilylethane. The second step has been discussed in some detail in the previous publication.[1]

Additional evidence in support of the reactions as given in these equations has been obtained. A pentenyltrichlorosilane was isolated from the reaction of 1-pentyne and trichlorosilane in the presence of peroxide. There are two isomeric pentenyltrichlorosilanes which could be obtained in this reaction, however, from a consideration of the boiling point data and previous reactions that have been conducted under similar conditions, it is believed that the isolated compound is 1-pentenyl-1-trichlorosilane, $CH_3CH_2CH_2CH{=}CH\text{-}SiCl_3$.[2] Isolation of this substituted vinyl addition product indicates that equation (1) is one step of the reaction. Thus, it is reasonable to assume that the reactions as outlined by equations 1 and 2 are indeed the reactions whereby disubstituted products are formed from an alkyne and trichlorosilane in the presence of a peroxide.

This furnishes another method of preparing alkenyltrichlorosilanes. Vinyltrichlorosilane has been prepared by the direct reaction of vinyl chloride and silicon[3] or by dehydrohalogenation of a mixture of α- and β-chloroethyltrichlorosilanes with anhydrous quinoline.[3]

Experimental

1-Pentenyl-1-trichlorosilane.—A mixture of 271 g. (2.0 *M*) trichlorosilane and 12.1 g. (0.05 *M*) of finely divided benzoyl peroxide was placed in a glass-lined autoclave. To this was added 34 g. (0.5 *M*) of 1-pentyne (Farchan Research Laboratory) in 50 g. of trichlorosilane. The mixture was heated at 80° for fifty-two hours under its own vapor pressure. Distillation of the reaction mixture gave in addition to the unused trichlorosilane 10.8 g. of 1-pentenyl-1-trichlorosilane, b. p. 85° (80 mm.) and 11.9 g. of less pure 1-pentenyl-1-trichlorosilane. A residue of 18.2 g. was obtained.

Anal. Calcd. for $C_5H_9SiCl_3$: Si, 52.26; unsaturation, 1 double bond per 205 g. Found: Si, 51.6; unsaturation (reaction with Br_2), 1 double bond per 246 g.[4]

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[2] Sommer, Pietrusza and Whitmore [THIS JOURNAL, **69**, 188 (1947); **70**, 484 (1948)] has shown that only 1-octyltrichlorosilane results from the addition of trichlorosilane to 1-octene in the presence of peroxide (99% yield).

[3] Hurd, *ibid.*, **67**, 1813 (1945).

[4] The author acknowledges the aid given by Dr. E. H. Winslow who determined the unsaturation.

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Viscosities of 2-Methyl-3-butyn-2-ol and 1,1-Dibutoxyethane

BY PHILIP J. ELVING,[1] NORMAN ALPERT AND PHILIP E. TOBIAS

The kinematic viscosities of 2-methyl-3-butyn-2-ol and 1,1-dibutoxyethane (acetaldehyde dibutyl acetal) were determined over the temperature range of 0 to 100°. A Fenske–Cannon–Ostwald viscosimeter (Series 50)[2] was used; distilled water was used to calibrate the viscosimeter. The accuracy of the data was limited by the constancy in temperature of the thermostat used, which was ±0.1°. The compounds were purified by careful rectification, and had these boiling point ranges and refractive indices: methylbutynol, 104 to 105°, $n^{20}\mathrm{D}$ 1.4203; dibutoxyethane, 188 to 189°, 1.4080.

The viscosities were calculated from the equation $V = Ct$, where V is the kinematic viscosity in centistokes, C is the calibration constant for the viscosimeter, and t is the efflux time in seconds. The viscosity in centipoises equals the product of the viscosity in centistokes and the density; for methylbutynol, d^{20}_{20} 0.8628 and d^{25}_{25} 0.8588; for the dibutoxyethane, d^{20}_{20} 0.8335 and d^{25}_{25} 0.8300.

Temp., °C.	Viscosity in centistokes	
	Methylbutynol	Dibutoxyethane
0	10.83	1.927
25	3.43	1.239
50	1.54	0.871
75	0.891	0.668
100	0.539	0.492

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[2] A. S. T. M. Method D445-46T.

PUBLICKER INDUSTRIES, INC.
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The Alkylation of Decalin with Ethylene[1,2]

BY J. R. DICE AND D. R. MCKINNEY[3]

The alkylation of decalin[4] with ethylene in the presence of aluminum chloride produces a complex mixture of products. From this mixture we have isolated a fraction which apparently contains some 2-ethyldecalin. The evidence for this is based on the isolation of derivatives of 2-ethylnaphthalene from the dehydrogenation products of the given fraction. Since the dehydrogenation procedure employed[5] has been shown not to effect skeletal rearrangement in various similar methyl decalins and octalins, it is reasonable that no skeletal rearrangements occurred in this case. Derivatives of some other compounds were also isolated, but none could be identified. That some of the original products are aromatic in nature is shown by the colors obtained on adding picric acid and trinitrobenzene solutions and by the

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[1] Presented at the Fourth Annual Southwest Regional Meeting of the American Chemical Society, Shreveport, Louisiana, December 10, 1948.

[2] Most of the equipment used in this investigation was purchased from funds provided by the Research Institute of the University of Texas, Project 186.

[3] From the M. A. thesis of D. R. McKinney, the University of Texas, 1948.

[4] Pertinate references to the alkylation of cycloalkanes are: (a) Ipatieff, Komarewsky and Grosse, THIS JOURNAL, **57**, 1722 (1935); and (b) Petrov, *Chimijatwerdogo Toplieva*, **5**, 632; *Chem. Zentr.*, **107**, I, 251 (1936).

[5] Linstead, Milledge, Thomas and Walpole, *J. Chem. Soc.*, 1146 (1937).