distillation was given further study in the case of benzohydryl trichloroacetate. When this ester was heated in a distilling flask under reduced pressure, a 70% yield of benzohydryl chloride was obtained. The identity of the benzohydryl chloride was established by analysis and by conversion to dibenzohydryl ether.[5] The decomposition also resulted in the evolution of hydrogen chloride and carbon dioxide. Quantitative determination of the hydrogen chloride in the evolved gases showed that nearly one-third of the chlorine in the ester could be accounted for in this way. No free chlorine could be detected in the gaseous products.

When the thermal decomposition of benzohydryl trichloroacetate was carried out at atmospheric pressure, the yield of benzohydryl chloride was reduced to 39% and a 17% yield of tetraphenylethylene was also obtained. The tetraphenylethylene is probably a secondary product of the decomposition, since its formation during the distillation of benzohydryl chloride at atmospheric pressure has been previously reported.[6]

Experimental

4-Chlorobenzohydrol and 4,4'-Dichlorobenzohydrol.—These alcohols were prepared in about 85% yield by reduction of the corresponding ketone with aluminum isopropoxide according to the procedure given by Wilds.[7] The authors are grateful to the Heyden Chemical Corporation for the sample of 4,4'-dichlorobenzophenone used in this work.

Benzohydryl Trichloroacetate.—Benzohydrol (18.4 g., 0.1 mole) and 18 g. (0.11 mole) of trichloroacetic acid were refluxed with 200 ml. of benzene in a flask attached to a water trap.[4] When the theoretical amount of water was collected, the solution was cooled and the unreacted trichloroacetic acid was removed by extraction with 10% sodium bicarbonate solution. The benzene was evaporated under reduced pressure and the remaining oil was taken up in 12 ml. of isoamyl acetate. The solution was kept at −5° for two days. The large crystals which formed were removed by filtration. The filtrate was concentrated to approximately two-thirds of its volume and placed in the refrigerator for two weeks. The resulting crystals were removed, combined with the first crop and recrystallized again from isoamyl acetate. The filtrate was concentrated in order to get good recovery of the product. It was necessary to pulverize the crystals in a mortar and dry them for 24 hours in a desiccator containing flaked paraffin in order to free them of isoamyl acetate. The product was then recrystallized from 95% ethanol to give 21 g. (63%) of benzohydryl trichloroacetate melting at 49.5–51°.

Anal. Calcd. for $C_{15}H_{11}Cl_3O_2$: C, 54.65; H, 3.36; Cl, 32.27. Found: C, 54.42; H, 3.24; Cl, 32.12.

4-Chlorobenzohydryl Trichloroacetate.—By the procedure outlined above 9 g. (0.055 mole) of trichloroacetic acid and 10.6 g. (0.05 mole) of 4-chlorobenzohydrol gave 8 g. (44%) of 4-chlorobenzohydryl trichloroacetate melting at 45–46°.

Anal. Calcd. for $C_{15}H_{10}Cl_4O_2$: Cl, 38.95. Found: Cl, 38.78.

4,4'-Dichlorobenzohydryl Trichloroacetate.—By the same method used for benzohydryl trichloroacetate, 8.4 g. (0.033 mole) of 4,4'-dichlorobenzohydrol and 6 g. (0.04 mole) of trichloroacetic acid gave 7.5 g. (57%) of 4,4'-dichlorobenzohydryl trichloroacetate melting at 59–59.5°.

Anal. Calcd. for $C_{15}H_9Cl_5O_2$: Cl, 44.48. Found: Cl, 44.43.

Pyrolysis of Benzohydryl Trichloroacetate.—Benzohydryl trichloroacetate was prepared as described above from 20 g. (0.1 mole) of benzohydrol and 18 g. (0.11 mole) of trichloroacetic acid. After removal of benzene, the residue was distilled under reduced pressure. Decomposition started immediately and a yellow liquid distilled slowly at 138–140° (3 mm.). The distillate was redistilled to give 14 g. (70%) of benzohydryl chloride.

Anal. Calcd. for $C_{13}H_{11}Cl$: C, 76.9; H, 5.44. Found: C, 76.55; H, 5.44.

The benzohydryl chloride was further identified by conversion to dibenzohydryl ether melting at 109°.[5]

In another pyrolysis, 25 g. (0.076 mole) of benzohydryl trichloroacetate was placed in a modified claisen flask fitted with a condenser for distillation. The flask was heated for 5 hours in a metal-bath at 280°. Some of the gas evolved was passed into barium hydroxide solution to give an immediate precipitate of barium carbonate. When the gas evolved was passed into water, the water produced a white precipitate of silver chloride when a few drops of silver nitrate solution was added. Chlorine could not be detected in the gaseous mixture by testing with potassium iodide and starch. The pressure in the distillation assembly was then reduced to 1.5 mm. and the flask was heated again. Benzohydryl chloride (4 g., 39%) was collected at 132–134° (1.5 mm.).

The tarry residue in the flask was removed by extraction with benzene after which the benzene was removed by evaporation and the residue was dried in an oven at 110°. The residue was then placed in a soxhlet extractor and extracted with methanol. The methanol was evaporated and the residue was recrystallized three times from benzene to give 2.1 g. (17%) of tetraphenylethylene, identified by melting point and mixed melting point with an authentic sample.

In another pyrolysis of benzohydryl trichloroacetate, analysis of the evolved gases showed that 31.6% of the total chlorine in the benzohydryl trichloroacetate was evolved as hydrogen chloride during the decomposition.

CHEMISTRY DEPARTMENT
STATE UNIVERSITY OF IOWA
IOWA CITY, IOWA

Prediction of Hydrocarbon Burning Velocities by the Modified Semenov Equation

BY P. L. WALKER, JR., AND C. C. WRIGHT

RECEIVED SEPTEMBER 26, 1952

The authors,[1] using the thermal theory of Semenov, and Simon,[2] using the diffusion theory of Tanford and Pease, have satisfactorily correlated the experimental burning velocities of a majority of the hydrocarbon–air mixtures investigated by assuming the specific reaction rate constants in the two equations independent of hydrocarbon. The predicted burning velocities of acetylene and ethylene, however, deviated markedly from experimental results for both theories. It was, therefore, concluded that the rate constants for the combustion of these hydrocarbons vary noticeably from all other hydrocarbons investigated.

In the previous correlation by the Semenov equation, due to lack of sufficient data, the energy of activation of all hydrocarbons for the combustion reaction was assumed to be 40 kcal./mole, which approximates the available low temperature data on the oxidation of hydrocarbons. Recent work by Fenn,[3] where he was able to associate lean limit flame temperatures of hydrocarbons with their activation energies, shows that high temperature activation energies for hydrocarbon combustion are considerably lower than the value of 40 kcal./

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[5] E. Wedekind and K. Schenk, *Ber.*, **44**, 201 (1911).

[6] O. Anselmino, *Ber. deut. pharm. Ges.*, **16**, 390 (1906).

[7] A. L. Wilds in Adams, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 203.

[1] P. L. Walker, Jr., and C. C. Wright, THIS JOURNAL, **74**, 3769 (1952).

[2] Dorothy Martin Simon, *Ind. Eng. Chem.*, **43**, 2718 (1951).

[3] John B. Fenn, *ibid.*, **43**, 2865 (1951).

mole taken from hydrocarbon oxidation data, and, furthermore, that ethylene and acetylene have activation energies markedly below those of the straight chain hydrocarbons. Using the new activation energies and experimental flame temperatures (which are thought by the authors to be preferable to adiabatic temperatures), the burning velocities of ethylene and acetylene relative to propane, as predicted by the Semenov equation, have been reevaluated, as shown in Table I.

TABLE I

MAXIMUM BURNING VELOCITIES OF HYDROCARBON FLAMES

Hydrocarbon	Vol. fuel, %	Activation energy,[3] kcal./mole	Exp. flame temp., °K.	Burning velocity cm./sec. Exptl.	Burning velocity cm./sec. Sem. eqn.
Propane	4.5	26.1	2158[a]	39.0[d]	39.0
Ethylene	7.4	23.6	2238[a]	68.3[d]	71.0
Acetylene	10.4	20.4	2480[b]	141.0[c]	152.5

[a] G. W. Jones, B. Lewis, J. B. Friauf and G. St. J. Perrott, THIS JOURNAL, **53**, 869 (1931). [b] H. Behrens and F. Rossler, *Z. Naturforsch.*, **5a**, 311 (1950). [c] O. Levine and M. Gerstein, *Natl. Advisory Comm. Aeronaut.*, RM E51JO5, 1951. [d] M. Gerstein, O. Levine and E. L. Wong, THIS JOURNAL, **73**, 418 (1951).

These new results give insight into the character of the variation of the specific reaction rate constant in the Semenov equation for ethylene and acetylene as compared to other hydrocarbons. The simplified Semenov equation[1] contains the specific reaction rate constant in the form, $k = Ke^{-E/RT}$. In the above correlation, the steric factor, K, by necessity is assumed independent of hydrocarbon, thus implying that variation in the specific reaction rate constant at a given temperature is simply due to a variation in the energy of activation. The fact that the above correlation is successful would seem to indicate that the steric factor of acetylene and ethylene for the combustion reaction is not greatly different from that of other hydrocarbons. It also emphasizes the important role which activation energy plays in determining the fundamental burning velocity of a hydrocarbon. Perhaps the major significance of the results, however, is that the activation energies of hydrocarbons determined from lean limit and ignition energy data bring the flame speed predictions into line with experimental results, suggesting that the same mechanism may be important in the different combustion phenomena.

DIVISION OF FUEL TECHNOLOGY
PENNSYLVANIA STATE COLLEGE
STATE COLLEGE, PA.

The Absence of Quaternary Salt Formation between Phosphoryl Chloride and Pyridine[1]

BY B. M. ZEFFERT, P. B. COULTER AND RUDOLPH MACY

RECEIVED SEPTEMBER 8, 1952

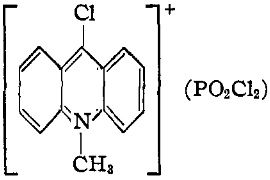
The Grignard reagent, RMgX, can be used to place alkyl or aryl groups on the phosphorus atom in $POCl_3$; when the reaction is conducted according to the normal procedure (addition of $POCl_3$ to the Grignard reagent in ether), all three chlorine atoms are replaced to produce phosphine oxides, R_3PO. It was shown[2] that one Cl atom can be blocked by the preliminary synthesis of an amido compound, $R_2N-POCl_2$, which can be isolated and put through the Grignard reaction, thus placing two R groups on the phosphorus atom.

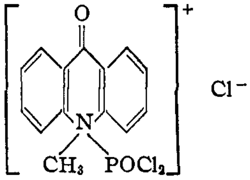
One Cl atom can also be blocked in Grignard reactions if the $POCl_3$ is first added to N-methylacridone to form a 1:1 complex salt.[3] This compound was isolated[3,4] and the authors presented evidence to show that salt formation (Formula I) occurs through interaction of $POCl_3$ and the carbonyl group of the acridone. Kosolapoff[5] later found that R_2POCl compounds are produced predominantly, in Grignard reactions of $POCl_3$ in ether solution, if pyridine is first added to the $POCl_3$ in equimolar amounts. He ascribed this effective blocking of one Cl atom to quaternary salt formation between pyridine and $POCl_3$ and reported the reaction as

$$POCl_3 + C_5H_5N \longrightarrow C_5H_5N(POCl_2)Cl \xrightarrow[(HOH)]{2RMgX} R_2PO_2H$$

Kosolapoff felt that the reactions described by Gleu and Schubert involved a similar quaternary nitrogen salt (Formula II) and that phosphonic acids, $RPO(OH)_2$, could be synthesized by this method if other complexes of pyridine and $POCl_3$ could be formed. He was unable to block two Cl atoms by doubling the ratio of pyridine to $POCl_3$ and suggested that the larger complexes might be stable only at low temperatures.[5] The existence of the 2:1 compound at normal temperatures had been reported previously[6] and later disputed with good evidence.[7]

The present work was initiated to determine the temperatures at which the postulated complex compounds of $POCl_3$ and pyridine exist, and thus to define conditions for the preparation of phosphinic and phosphonic acids in good yields by means of the Grignard reaction.


Formula I


Formula II

Materials.—The $POCl_3$ used was distilled at 106.5–106.9° from a sample of Mallinckrodt Analytical Reagent material. The freezing point of the distillate was 1.02°; literature values are: b.p. 106.4–106.7°, f.p. 1.17°.[8]

The pyridine was obtained from the Eastman Kodak Co. and distilled over barium oxide prior to use; b.p. 114–115.5°, f.p. −42.3°, $n^{25}D$ 1.5061; literature values are: b.p. 115.5°[9]; f.p. −42.0°[10]; $n^{25.2}D$ 1.5070.[11]

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[1] Abstracted from an M.S. thesis submitted by B. M. Zeffert to the Graduate School, University of Maryland.

(2) G. M. Kosolapoff, THIS JOURNAL, **71**, 369 (1949).

(3) K. Gleu and A. Schubert, *Ber.*, **73**, 805 (1940).

(4) K. Gleu, S. Nitzsche and A. Schubert, *ibid.*, **72**, 1093 (1939).

(5) G. M. Kosolapoff, THIS JOURNAL, **72**, 5508 (1950).

(6) D. R. Boyd and D. E. Ladhams, *J. Chem. Soc.*, 215 (1928).

(7) W. Gerrard, *ibid.*, 106 (1945).

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