the product evidently was not sufficiently stable, at that temperature, to be saved.

The author wishes gratefully to acknowledge the courtesy of Professor H. I. Schlesinger, in whose private laboratory the major portion of this experimental work was done.

Summary

Methylboric acid, $CH_3B(OH)_2$, a volatile and unstable compound (not previously isolated) has been prepared and characterized. A thorough study of its dissociation, according to the equation $3CH_3B(OH)_2 \rightarrow (CH_3BO)_3 + 3HOH$, gave the result $\Delta F° = 9300 - 22.3\ T$, for the reaction in the vapor phase.

The anhydride of methylboric acid, $(CH_3BO)_3$ (b. p. 79°, m. p. −38°), is a ring trimer for whose thermal dissociation no evidence was found. It forms a mono-trimethylaminate, whose triple point is 67°, and (extrapolated) boiling point, 131° (highly dissociated vapor). No higher aminates are formed. A mono-ammoniate is formed, and a far less stable di-ammoniate; the latter evidently is formed by hydrogen bonding. It appears that only one boron atom (of the three in the ring) can coördinate with an external electron-donor atom.

The ring of methylboric anhydride is split by the action of boron trifluoride, to form the new compound methylboron difluoride (b. p. −62.3°, m. p. −130.5°), in excellent yields and without troublesome impurities. By the analogous cleavage of dimethylboric anhydride, another new compound, dimethylboron fluoride (b. p. −42.2°, m. p. −147.4°) is produced, also in good yields and in satisfactory condition. Both of these compounds appear to be permanently stable at room temperature.

LOS ANGELES, CALIFORNIA RECEIVED APRIL 29, 1940

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

The Effect of Surface on Cool Flames in the Oxidation of Propane

BY R. A. DAY, JR., AND R. N. PEASE

The occurrence of successive "cool flames" during the oxidation of paraffin hydrocarbons is one of the many puzzling features of these reactions. The observations are of this sort. With a 1:1 propane–oxygen mixture, at about 400 mm. and 300°, in a 3.5-cm. Pyrex or silica tube, there will be first an induction period of perhaps five minutes duration; the pressure will then begin to rise slowly, and after several seconds a faint bluish luminescence will be seen near the center of the tube. This spreads toward the ends of the tube and then fades away in a few seconds. The phenomenon will be repeated several seconds later and at intervals until, in all, one may observe as many as eight or nine such periods of luminescence in the space of a minute or more. Coincident with each cool flame, a fairly sharp pressure rise occurs which is partially corrected in the succeeding period of quiescence.

It is to be emphasized that both the onset and the duration of the cool flames occupy measurable times. The phenomenon is sharply distinguished from the ignition which occurs at somewhat higher pressures with a bright yellow luminescence and the characteristics of a mild explosion.

It is evident that during the intervals between cool flames some intermediate is building up to a minimum concentration sufficient to produce the unstable state which leads to partial inflammation. Newitt and Thornes[1] suggest as a result of analyses conducted at different points in the process that the substances which are responsible are the "higher aldehydes," presumably acetaldehyde and propionaldehyde. These substances were shown to rise to a maximum concentration before the flame and to fall thereafter. On the other hand, Aivazov and Neumann[2] stress the importance of peroxides, and Neumann and Toutakin[3] go on to show that diethyl peroxide will in fact induce cool flames in butane–oxygen mixtures. However, similar experiments by Harris and Egerton,[4] in which propane was substituted for butane, revealed that even the ignition of diethyl peroxide failed to induce reaction in the propane–oxygen mixtures.

It is with this last result that we are especially

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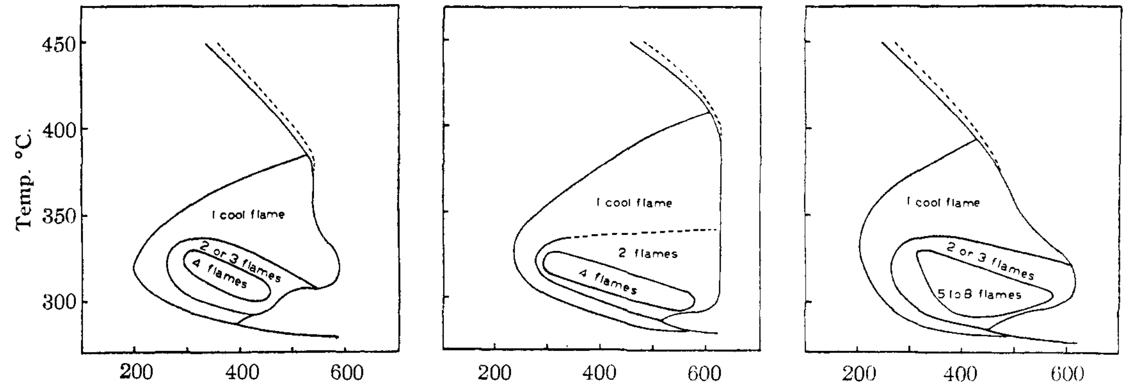
[1] Newitt and Thornes, *J. Chem. Soc.*, 1656, 1665, 1669 (1937).

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

[3] Neumann and Toutakin, *Compt. rend.*, **205**, 278 (1937).

[4] Harris and Egerton, *Proc. Roy. Soc.* (London), **A168**, 1 (1938).



Pressure, mm. Nitric acid treated.

Pressure, mm. Potassium chloride treated.

Pressure, mm. Hydrofluoric acid treated

Fig. 1.—Cool flames in 1:1 propane–oxygen mixtures.

concerned. Earlier work[5] had shown that by coating a Pyrex reaction vessel with potassium chloride the yield of peroxides could be largely suppressed without materially altering the rate of oxidation of the propane. This again indicates that peroxides are not essential to the oxidation. Thus one might expect to observe cool flames in a salt-treated vessel as well as in a clean one. As a matter of fact, Newitt and Thornes[1] state that this is the case but do not give details.

It was for the purpose of confirming this conclusion and obtaining some first-hand information on cool flames that this investigation was undertaken. In addition we were interested in determining the effects of etching the Pyrex reaction tube with hydrofluoric acid. This might be thought of as a more radical "cleaning" of the surface than is produced by the hot concentrated nitric acid usually employed by us. According to Kowalski and co-workers,[6] the oxidation of ethane is markedly accelerated when a silica reaction tube is etched with hydrofluoric acid. Further, it was found by Snowden and Style[7] that etching diminishes for a time the rate of oxidation of formaldehyde. These observations suggested that the oxidation of propane might be considerably altered in an etched tube.

Our experimental data are in two parts. We have sketched in the cool flame region for a 1:1 propane–oxygen mixture in Pyrex tubes which were (1) etched with hydrofluoric acid, (2) cleaned with hot concentrated nitric acid, and (3) rinsed with potassium chloride solution. In addition we have determined some of the products of oxidation (flow method) as affected by pretreatment of the reaction tube, special attention being given to the peroxide yield.

The experiments on the cool flame region were run with Pyrex reaction tubes 3.5 cm. in diameter and 15 cm. long. One such tube was filled with hydrofluoric acid solution and allowed to stand for an hour; the second was boiled out with concentrated nitric acid and rinsed with water; the third was filled with a 20% potassium chloride solution and allowed to stand overnight, after which it was drained. The tubes were mounted vertically in an electrically heated air-bath which was provided with a glass window. Connections were made with sources of propane and oxygen, with a manometer, and with a Hyvac pump; a liquid-air trap being interposed. Evacuation was not exhaustive. The gases were not pre-mixed, propane being first admitted to the desired pressure and then oxygen.

The results are presented graphically in Fig. 1, which consists of plots of total pressure against temperature for each of the three reaction tubes. The region above and to the right of the curves represents ignition, whereas that below the curves and to the left represents slow reaction. The central part of each figure comprises a set of roughly concentric areas within which a number of successive cool flames was observed, as indicated. The narrow strips adjacent to the ignition curves at higher temperatures, represented by dotted lines, define the region in which the bright blue flames, observed by Newitt and Thornes,[1] were formed. On passing to slightly higher pressures, these change to the true yellow ignition flames.

[5] Pease and Munro, THIS JOURNAL, **56**, 2034 (1934).

[6] Kowalski, *et al.*, *Physik. Z. Sowjet Union*, **1**, 451 (1932).

[7] Snowden and Style, *Trans. Faraday Soc.*, **35**, 426 (1939).

The most casual examination is sufficient to show that there was very considerable uniformity in behavior in the three bulbs, although there were minor differences. Thus in the etched tube there were more successive flames at the peak of the performance, and at 325° and above ignition occurred at somewhat lower pressures. In the "nitric acid" tube, the area of the cool flame region appeared to be distinctly smaller than in either of the others. In the "potassium chloride" tube, the induction period was much more pronounced at lower temperatures. However, one may say that on the whole the qualitative behavior was the same in all three tubes. Moreover, the results are similar to those obtained by Newitt and Thornes[1] with a silica tube. It thus appears that the nature of the surface has no great effect on the cool flame and ignition characteristics of the reaction.

In contrast to the above is the effect of surface treatment on the peroxide yield (Table I).[8] As mentioned above, there are only traces of peroxide from a potassium chloride treated tube, whereas substantial yields are obtained after washing with nitric acid or light etching with hydrofluoric acid.[9]

TABLE I

EFFECT OF SURFACE TREATMENT ON PRODUCTS OF OXIDATION

Flow experiments at 375° and 1 atm.; 1:1 propane–oxygen at 40 cc./min.; reaction tube 50 cc.

Treatment of surface	For 100 cc. propane entering								
	Reacted, cc.		Formed, cc. gas or vapor						
	C_3H_8	O_2	R_2O_2	C_3H_8	CO	H_2O	C_2H_4	CO_2	H_2
H_2F_2	53	98	16	14	54	74	4	6	5
HNO_3	55	98	14	13	63	69	5	6	3
KCl	64	96	nil	13	52	69	5	15	(14)

The lack of correlation between the occurrence of cool flames and the formation of peroxides might incline one to accept Newitt's view that higher aldehydes are the effective agents, but there are difficulties here also. Thus, at somewhat lower temperatures (∼100°), the oxidation of acetaldehyde is strongly accelerated after a potassium chloride treatment.[10] Assuming that other aldehydes behave similarly, it would follow that a minimum concentration of aldehyde would be set up with greater difficulty in the salt-coated tube. Cool flames should therefore form less readily. On the other hand, etching tends to diminish the rate of oxidation of formaldehyde,[7] so that in an etched bulb aldehydes might be expected to collect and to promote cool flame formation. Nevertheless, the effects of etching and of potassium chloride are minor.

Lewis and von Elbe[11] also turn to aldehydes as the source of chain carriers responsible for hydrocarbon oxidation. A branching process producing many hydroxyl radicals is supposed to occur.[12] Chain carriers are destroyed at the walls, but the authors conclude that the rate of this process is determined less by the activity of the walls than by the rate of diffusion of carriers through the surrounding gas. Hence they look for little effect of changes in the nature of the walls. Repeated cool flames and the failure of ignition to follow cool flame formation are attributed to the setting-up of convection currents in the gas due to local self-heating. This allows more efficient contact with the walls, and hence promotes extinction of chains. These characteristics of cool flame processes are thus referred to the physical processes of diffusion and convection.

Although it cannot be denied that these physical processes are of importance in determining ignition characteristics, there is another feature of hydrocarbon oxidation which may be operative in the cool flame region. This is the occurrence of a maximum and a minimum in the rate–temperature curve at lower pressures, and hence of a region of negative temperature coefficient.[13] It appears that in this region (325–375°) a new and efficient chain-breaking reaction is coming into prominence. It is obvious that as this region is entered by self-heating of the reaction mixture, it provides an effective brake on uncontrolled development of the reaction. The occurrence of cool flames as a distinct observable phenomenon may therefore be incidental to the existence of this region of negative temperature coefficient of the rate.

As to the particular reactions involved in the cool flame region, little can be said at present. Cool flame spectra in such substances as hexane and acetaldehyde have been identified with a formaldehyde fluorescence spectrum,[14] indicating the presence of some excited formaldehyde mole-

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(8) For analytical methods, see ref. 5, and Day and Pease, THIS JOURNAL, **61**, 524 (1939). Values for aldehydes and alcohols are not given owing to uncertainties due to the presence of peroxides.

(9) Heavy etching sometimes cuts down the peroxide yield, and in one case there was no reaction at all up to 450°. In another case, repeated coating with potassium chloride prevented reaction up to 520°, where ignition occurred.

(10) Pease, THIS JOURNAL, **55**, 2753 (1933).

(11) Lewis and von Elbe, "Combustion, Flames and Explosions of Gases," Cambridge University Press, 1938, Chap. IV; also, personal communication from Drs. Lewis and von Elbe.

(12) Ref. 11, p. 115.

(13) Pease, THIS JOURNAL, **51**, 1839 (1929); **60**, 2244 (1938).

(14) Ubbelohde, *Proc. Roy. Soc.* (London), **152A**, 354 (1935).

cules. In view of the weakness of the radiation, this conclusion may have only minor significance even though the flame itself is observed on this account. There is evidence[15] that the eye is sensitive to as little as 10^{-9} erg per second in the blue-green, corresponding to about 200 quanta per second. Since about 10^{18} molecules are reacting per second, only a vanishingly small fraction of elementary processes result in radiation.

(15) Wentworth, *Psychological Monographs*, **40**, pp. 136, etc. (1930).

Summary

The cool flame region in 1:1 propane–oxygen mixtures is not materially affected by etching the reaction tube or coating it with potassium chloride. It is thus determined by conditions in the gas phase. Attention is drawn to the region of negative temperature coefficient of the rate as an effective control, leading to successive flames and preventing ignition.

PRINCETON, NEW JERSEY RECEIVED JANUARY 20, 1940

[CONTRIBUTION FROM METCALF RESEARCH LABORATORY, BROWN UNIVERSITY]

Properties of Electrolytic Solutions. XXII. Conductance of Ethylene Dichloride Solutions of Some Quaternary Ammonium Salts Having Large Negative Ions[1]

BY D. LEIGH FOWLER AND CHARLES A. KRAUS

In earlier papers of the present series, the behavior of solutions of electrolytes in different solvents has been sketched in broad outline. It has been shown that the properties of dilute solutions of typical electrolytes are accounted for rather satisfactorily through a combination of the ion-atmosphere theory of Debye and Hückel and Onsager with the ion-association theory of Bjerrum. The properties of dilute electrolyte solutions are dependent upon the temperature, the dielectric constant and the viscosity of the solvent medium and the size of the ions. In order to elucidate more fully the phenomena characteristic of electrolytic solutions, further knowledge is required concerning specific factors such as the constitution and configuration of the ions and their interactions with one another and with the solvent molecules. In certain cases, interactions between the ions and polar molecules other than those of the solvent are also of interest.

The present paper is the first of a series dealing with the conductance of various types of electrolytes when dissolved in ethylene dichloride, pyridine and nitrobenzene. The dielectric constants of these solvents are 10.23,[1a] 12.01[2] and 34.50,[3] respectively. None of these solvents has an active hydrogen atom and only pyridine has pronounced basic properties. All these solvents permit of accurate determination of Λ_0 values.

The present paper is primarily concerned with the determination of ion conductances in ethylene dichloride. In this, as in most nonaqueous solvents, reliable transference measurements cannot be made. Accordingly, it is necessary to resort to other means for approximating limiting ion conductances. It is well known that the mobility of ions, containing a large number of carbon atoms, decreases with increasing number of such atoms and that the decrease per atom decreases as the number of atoms increases. By introducing a large, and approximately equal, number of carbon atoms into the two ions of an electrolyte, these ions will have very nearly the same mobility and, accordingly, the limiting conductance of each ion will be one-half that of the electrolyte. Combining these ions with other ions and determining the Λ_0 values, the conductance of other ions may be approximated.

In an earlier paper,[4] it was shown that the fluoride and hydroxyl ions form stable complexes with triphenylboron and several quaternary ammonium salts of these ions have been described. To determine the ion conductance, we have measured the conductance of solutions of tetrabutylammonium triphenylborofluoride and tetrabutylammonium triphenylborohydroxide. We have also measured the conductance of several tetramethylammonium salts of the same ions.

II. Experimental

Solvent.—For the present investigation, ethylene dichloride was employed as a solvent. The method of puri-

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[1] This paper is based on a portion of a thesis presented by D. L. Fowler in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Brown University, 1935.

[1a] G. S. Hooper, Thesis, Brown University, 1933.

(2) Le Fèvre, *J. Chem. Soc.*, 776 (1936).

(3) Lattey and Gattey, *Phil. Mag.*, **7**, 985 (1929).

(4) Fowler and Kraus, THIS JOURNAL, **62**, 1143 (1940).