[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE OHIO STATE UNIVERSITY]

The Production of Hydrazine by the Reaction of Chlorine with Anhydrous Ammonia[1]

By ROBERT MATTAIR AND HARRY H. SISLER

The formation of hydrazine in appreciable yields by the direct reaction of chlorine with anhydrous ammonia has been demonstrated. The reaction was carried out in three ways: (a) the reaction of gaseous chlorine with liquid ammonia; (b) the reaction of a solution of carbon tetrachloride with liquid ammonia; and (c) the reaction of gaseous chlorine diluted with nitrogen, with gaseous ammonia followed by condensation of the gaseous products to the liquid state. The reaction occurs in two steps, the first fast and the second slow. $Cl_2 + 2NH_3 \rightarrow NH_2Cl + NH_4Cl$; $NH_2Cl + 2NH_3 \rightarrow NH_2NH_2 + NH_4Cl$. A possible explanation for the slowness of the second step and for the manner in which the yield of hydrazine depends upon the presence of a large excess of ammonia is presented.

The Raschig[2] process for the production of hydrazine, which is the basis for currently used industrial processes, involves the conversion of chlorine to hypochlorite by reaction with aqueous alkali, the ammonolysis of the hypochlorite in aqueous ammonia, and the reaction of chloroamine with aqueous ammonia to yield hydrazine.

We have found that anhydrous ammonia, under proper conditions, may be oxidized by chlorine almost completely to chloroamine, and the latter caused to undergo ammonolysis in anhydrous liquid ammonia to give hydrazine in considerable yields. We have been able to ameliorate the vigor of the reaction by diluting the chlorine with an inert gas, or by dissolving it in an inert liquid. It is possible to avoid the formation of nitrogen trichloride by the use of an excess of ammonia. In all, three methods for carrying out the reaction were tried.

Experimental

Methods of Analysis.—The various reaction products were analyzed for hydrazine by the benzalazine method. The chloride analyses were carried out by the gravimetric silver chloride method with all the customary precautions.

The Reaction of Chlorine with Liquid Ammonia.—Several experiments were carried out in which gaseous chlorine at atmospheric pressure was passed into liquid ammonia at a temperature of about $-33°$. The reactions were so extremely vigorous and such dense clouds of ammonium chloride filled the reaction vessel that this procedure was considered to be undesirable. Even in these cases, however, the analytical results indicated that hydrazine was formed, but in yields not exceeding a few per cent. based upon the chlorine used. One reaction was carried out at $-75°$ with similar results.

In an attempt to reduce the vigor of the reaction of chlorine with ammonia the chlorine was dissolved in carbon tetrachloride before addition to the ammonia. The apparatus used in this series of experiments is shown in Fig. 1. The Dewar flask A was attached to a tank of liquid ammonia and the requisite amount of the liquid drawn directly into the flask. The solution of chlorine in carbon tetrachloride was placed in the dropping funnel M cooled by a mixture of chloroform and carbon tetrachloride (L) kept at about $-30°$ by occasional addition of lumps of Dry Ice. The exit tube N was connected to a trap cooled by a Dry Ice–chloroform–carbon tetrachloride-bath. The chlorine–carbon tetrachloride solution was slowly added to the ammonia with constant stirring. The reaction was still quite vigorous, though less so than in the experiments described above. The formation of white clouds of ammonium chloride was observed. Whenever the addition of the chlorine solution to the reaction mixture was moderately fast, some of the ammonium chloride would leave the outlet tube of the trap; in these instances, the exit gases had a strong hypochlorite odor which later experiments showed to be due to chloroamine. At the end of the run the dropping funnel was

rinsed into the reaction vessel with carbon tetrachloride and stirring was continued for a short period of time. The apparatus was then disconnected at point O and the contents of the Dewar flask and of the trap were allowed to stand overnight so that the excess ammonia might evaporate.

LIQUID PHASE APPARATUS

A: Liquid Ammonia
B: Unsilvered Dewar
C: Glass Rod Stirrer
D: Cl_2-CCl_4 Delivery Tube
E: Glass Stirrer Sleeve
F: Rubber Stopper
G: Gum Rubber Sleeve
H: Electric Motor
I: Pressure Equalizing Dropping Funnel
J: Stopcock
K: $^{24}/_{40}$ Tapered Joint
L: $CHCl_3$-CCl_4-Dry Ice
M: Cl_2 In Inert Solvent
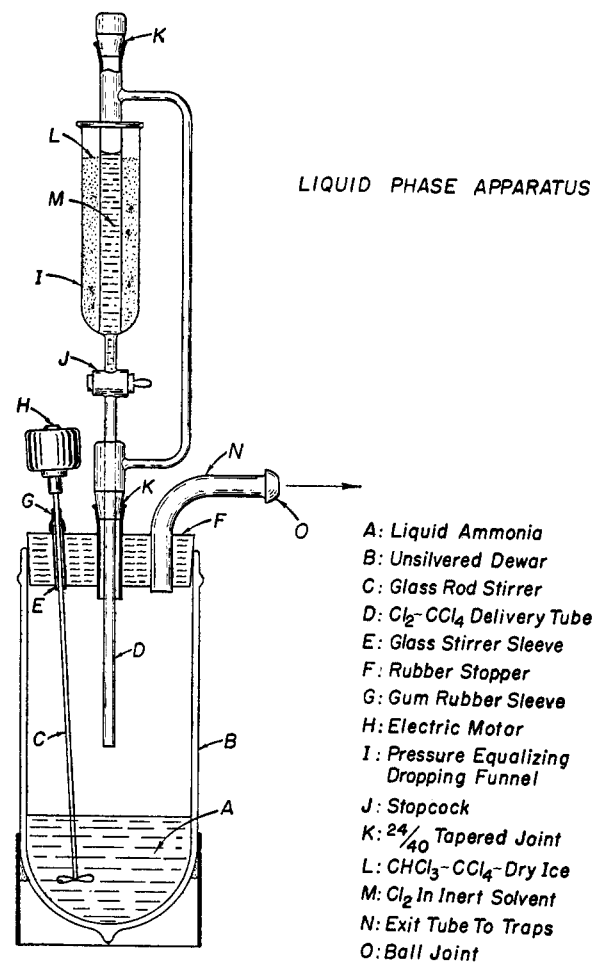N: Exit Tube To Traps
O: Ball Joint

Fig. 1.

After the excess ammonia had evaporated, water was added to the combined mixture of white solid and carbon tetrachloride which was found in the reaction flask and trap. The resulting water and carbon tetrachloride liquid phases were then separated, and the latter was washed several times with water. The combined aqueous portions were than analyzed for their hydrazine content. Results of some typical runs are recorded in Table I.[3]

It was discovered during these experiments that the length of time that the reaction mixture was allowed to stand has an important effect upon the yield of hydrazine. In the experiments above the reaction mixture was allowed to

(1) Presented at the September, 1950, Meeting of the American Chemical Society.

(2) F. Raschig, "Schwefel and Stickstoffstudien," Verlag Chemie G.m.b.H., Leipzig, Berlin, 1924.

(3) Similar experiments using bromine instead of chlorine gave no hydrazine.

TABLE I

Cl₂, g.	CCl₄, g.	NH₃, ml.	Mole ratio NH₃/Cl₂	Yield of N₂H₄ based on Cl₂, %
6.7	66	266	110/1	9.1
6.0	100	250	120/1	6.8
4.6	55	200	120/1	10.4
4.0	40	195	140/1	6.1
4.7	57	150	90/1	4.3
19.8	112	240	35/1	2.2

stand overnight to evaporate. In two experiments where the excess ammonia was immediately evaporated rapidly under reduced pressure, no hydrazine at all was obtained. These findings would indicate that the reaction proceeds in two steps (see below).

The Reaction of Chlorine and Ammonia in the Gas Phase. —When the pure gaseous chlorine and gaseous ammonia are brought together under ordinary pressure a highly vigorous reaction takes place. If, however, the chlorine gas is diluted with nitrogen prior to its being introduced into the ammonia, a smooth reaction occurs. Studies on this reaction were carried out in the apparatus shown in Fig. 2.
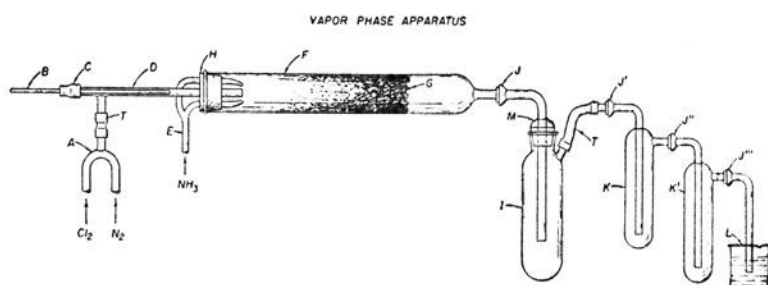
VAPOR PHASE APPARATUS

Fig. 2.—A, Cl₂–N₂ mixing tube; B, glass ramrod; C, pure gum rubber sleeve; D, Cl₂–N₂ delivery tube; E, NH₃ delivery tube; F, reaction tube; G, glass wool; H, rubber stopper; I, first trap, large; J, ball joint; K, small trap; L, beaker containing distilled H₂O; M, ³⁴/₄₅ tapered stopper; T, Tygon tubing.

The reaction chamber F was made of 50-mm. Pyrex tubing and was about 3 ft. in length. A ramrod B consisting of a piece of 6-mm. glass rod was provided for freeing the chlorine–nitrogen delivery tube of ammonium chloride plugs which tend to form at this outlet. I, K and K' are traps, cooled in a Dry Ice, chloroform and carbon tetrachloride mixture. Traps K and K' were necessary because experience showed that the chloroamine formed in the reaction tube is not completely absorbed or condensed in the first trap I. The distilled water trap was used to collect chloroamine which failed to condense in the three traps. The end of the reaction tube was filled with glass wool (G) which thoroughly trapped the ammonium chloride formed in the gas phase reaction. Flowmeters used for measuring the flow of nitrogen and ammonia are not shown in the figure. No flowmeter was used for the chlorine, the amount of chlorine passing into the reaction chamber during a run being determined by the loss in weight of a small stainless steel tank which contained the chlorine. The rate of flow could be controlled by observing the bubbling in the sulfuric acid wash bottle.

A typical experiment was carried out as follows. The apparatus was assembled without cooling the traps, without the distilled water at the end of the train, and with the chlorine–nitrogen inlet closed off. A stream of ammonia gas was then passed through the system to remove traces of moisture. Next trap K' was cooled to −80° and ammonia condensed in it until the liquid level was slightly above the bottom of the inside tube. This trap was then disconnected, tightly closed, and set aside in the coolant, while ammonia was condensed in the second trap in the same way. When filled above the level of the inlet tube it too was tightly closed and set aside in the coolant, and the flow of ammonia was stopped. Meanwhile the sulfuric acid wash bottle through which the chlorine was to be passed had been saturated with chlorine and the chlorine and nitrogen inlets were connected to A.

All connections were tightened, and the flow of nitrogen was started and the flow rate adjusted. The distilled water trap was placed at the end of the train. The flow of am-

monia and chlorine was then started and the flow rates rapidly adjusted. During an experiment, minor adjustments to keep gas flow rates as constant as possible were made. Each experiment was timed to within 15 seconds. During a run the reaction tube becomes warm near the region of mixing. It was estimated that the highest temperature attained in any experiment was between 40 and 50°.

At the end of each run the distilled water trap was removed, the flow of ammonia and chlorine was stopped simultaneously and, with the nitrogen still flowing, the apparatus was disconnected between traps I and K. The traps were corked immediately and allowed to stand for at least 12 hours in the coolant, after which they were opened and removed from the coolant, and the excess of ammonia was allowed to evaporate. The solid residues thus obtained were dissolved in water and the solutions analyzed for hydrazine and for chloride ion. The contents of traps K and K' were analyzed together. The contents of the distilled water trap were likewise analyzed for chloride. The reaction tube with its glass wool plug was thoroughly washed with water and the washings were analyzed for chloride.

The results of a typical series of experiments carried out in the manner described above are listed in Table II and plotted in Fig. 3. Some of these experiments were carried out before traps K and K' had been added to the system, so in these runs only the yields of hydrazine in trap I are listed. The yield of hydrazine in each case is based upon the chlorine used. The mole ratio of nitrogen to chlorine in these experiments was approximately 16.5 to 1.
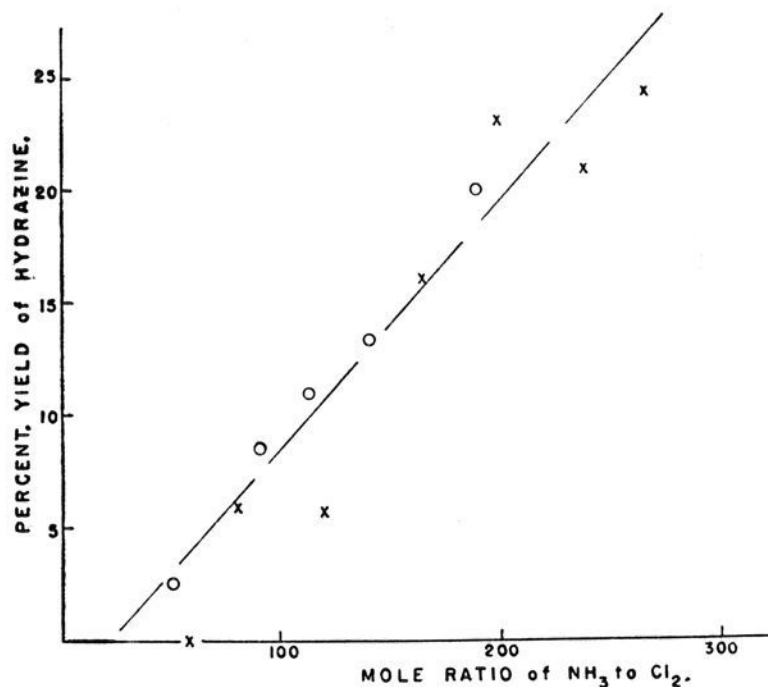

Fig. 3.—Yield of hydrazine in trap I vs. mole ratio NH₃/Cl₂: O and × refer to two series of experiments.

The results of the experiments listed in Table II and plotted in Fig. 3 indicate that the yield of hydrazine varies markedly with change in the mole ratio of ammonia to chlorine. In order to determine whether this effect is primarily on the reaction in the reaction tube or on the reaction in the traps, some experiments were carried out in which known quantities of ammonia were added to trap I before the run was started. The results of some experiments of this type are listed in Table III.

In several instances the solid formed in the reaction tube was tested for the presence of hydrazine and chloroamine. All such tests were negative. The solid was quantitatively analyzed for nitrogen and chlorine, and shown to be pure ammonium chloride. The gaseous products which were discharged from the reaction tube were found, however, to give strong positive tests for chloroamine (Palin[4] test).

Furthermore, an anhydrous ethereal solution of chloroamine was prepared from this gaseous mixture by the following procedure. Anhydrous ether was placed in trap I before the reaction was started and the gaseous reaction products were condensed on top of it. Two liquid layers are then obtained. The trap was then allowed to warm up and the excess ammonia to evaporate. The white solid which remained was filtered from the ether layer, leaving an

(4) A. Palin, *Analyst*, **20**, 207 (1945).

TABLE II

Expt.	Dura-tion of expt.[b] (min.)	Cl₂, g.	Mole[a] ratio NH₃/Cl₂	Yield of N₂H₄, %			Total chlorine removed as chloride, %				
				Trap I	Traps K, K'	Total	Reaction tube	Trap I	Traps K, K'	Water trap	Total
I	50	4.79	58/1	Negl.	5.5	5.5	54.8	29.0	8.7	1.8	94.3
II	60	5.85	52/1	2.4	...	..	51.3	..	..	..	..
III	50	5.26	81/1	5.8	7.8	13.6	53.4	30.2	10.5	1.4	95.5
IV	40	3.90	120/1	5.7	8.5	14.2	51.5	30.6	9.7	0.6	92.4
V	60	6.92	142/1	13.2	...	..	53.5	..	..	...	..
VI	45	5.02	189/1	19.9	...	..	50.1	..	..	...	..
VII	45	4.76	200/1	23.2	4.3	27.5	51.0	34.2	8.1	1.1	94.4
VIII	34	3.47	239/1	21.2	5.0	26.2	52.8	34.5	8.2	1.0	96.5
IX	32	3.24	267/1	24.2	6.3	30.6	49.1	36.2	8.1	1.1	94.5

[a] This mole ratio refers to the gases in the reaction tube and approximately to the trap I, which contained no ammonia at the start of the runs. [b] I.e., the duration of the gas phase reaction.

TABLE III

| Expt.		X	XI	XII
Duration of expt., min.		60	40	30
Chlorine, g.		5.83	4.02	3.01
Mole ratio of NH₃/Cl₂	In gas	88/1	85/1	85/1
	Total in Trap I	214/1	254/1	365/1
Yield of N₂H₄, %	Trap I	17.4	19.3	23.7
	Traps K,K'	....	6.8	8.9
	Total	....	26.1	32.7
Total chlorine removed as chloride, %	Reaction tube	51.9	53.6	53.0
	Trap I	....	29.8	29.0
	Traps K,K'	....	10.0	10.9
	H₂O	....	2.0	1.8
	Total	....	95.4	94.7

ethereal solution of chloroamine containing some ammonia. On standing in a closed bottle a white solid, presumably ammonium chloride, was slowly deposited, but after 3 days the solution still gave a strong test for chloroamine.

In order to be certain that the 12-hour period of standing at Dry Ice temperatures is sufficient for all the chloroamine to react with the liquid ammonia, the condensates in traps I, K and K' were in several instances tested for the presence of chloroamine after standing for 12 hours but before the ammonia was allowed to evaporate. Such tests were all negative, showing that the chloroamine had completely reacted.

Since studies of the Raschig synthesis of hydrazine have revealed that the yield of hydrazine is reduced in the presence of considerable concentrations of ammonium ion in the reaction liquor, it seemed interesting to test for a similar effect in this reaction. Experiments were, therefore, carried out in the manner described above, except that prior to the start of the run, weighed quantities of ammonium chloride were added to trap I. In one experiment the added ammonium chloride amounted to 0.4 mole per 1000 g. of ammonia in trap I. The mole ratio of ammonia to chlorine had been 200 to 1. The yield of hydrazine obtained from trap I was 11.2%, as compared with about 20% to be obtained from the results tabulated in Table II and plotted in Fig. 3. In another experiment in which the ammonia to chlorine ratio was 226 to 1, 0.2 mole of ammonium chloride per 1000 g. of ammonia was added to trap I. The yield of hydrazine in trap I was reduced from an expected 22 to 14.9%.

Discussion and Conclusions

The principal result of this work has been to demonstrate (a) that chlorine, diluted with an inert gas, reacts directly with anhydrous ammonia to produce chloroamine in high yields, and (b) that, under proper conditions, chloroamine reacts slowly with an excess of liquid ammonia to produce hydrazine in considerable yields. These processes may be represented by the equations

$$2NH_3 + Cl_2 \longrightarrow NH_2Cl + NH_4Cl \qquad (a)$$
$$NH_2Cl + 2NH_3 \longrightarrow NH_2NH_2 + NH_4Cl \qquad (b)$$
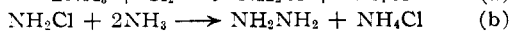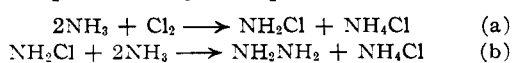
Conclusion (a) is supported by the facts that only slightly more than 50% of the total chlorine remained in the reaction tube as NH₄Cl, that no hydrazine was found in the reaction tube, and that abundant chloroamine, but no chlorine, was found in the effluent gases.

The low speed of step (b) in the reaction is analogous to that of the corresponding step in the Raschig synthesis. We have concluded that the reason for the slowness of this reaction lies in the electrical character of the halogen in the haloamine molecule. Unless the halogen is definitely negative, we may assume that ammonolysis would not result in the production of hydrazine, as

$$H^+\!-\!|\!-\!NH_2^-$$
$$X^-\!-\!|\!-\!NH_2^+$$
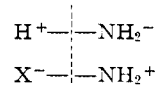
but would occur thus

$$H^+\!-\!|\!-\!NH_2^-$$
$$NH_2^-\!-\!|\!-\!Cl^+$$
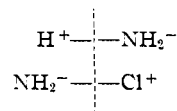
and would result in an exchange reaction. This hypothesis is supported by the experimental facts that fluoroamine reacts with aqueous ammonia to give good yields of hydrazine,[5] and that bromine was found by us to give no detectable trace of hydrazine on reaction with liquid ammonia. Since the chloroamine molecule is undoubtedly of low polarity, we have an explanation for the fact that the reaction to yield hydrazine has a rather high energy of activation, and thus is slow. This allows the nitrogen-producing side reaction discussed below to compete effectively.

An important yield-reducing reaction in the Raschig synthesis is

$$2NH_2Cl + N_2H_4 \longrightarrow N_2 + 2NH_4Cl$$
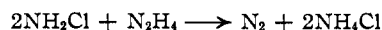
It is known further that ammonium ion affects the yield. Our results in liquid ammonia, as far as they go, indicate a similar situation. The fact that we obtained little hydrazine at ammonia to chlorine ratios of less than 50 to 1, whereas a ratio of approximately 20 to 1 gives maximum yields in the Raschig synthesis, may be explained as resulting from the necessity of maintaining a dilute solution for the ammonolysis of the chloroamine so as to

(5) O. Krefft, French Patent 735,020; C. A., 27, 1118 (1933).

reduce the speed of the hydrazine-destroying re-action and thus to favor the slower hydrazine-producing process. In the anhydrous system the ammonia functions not only as reactant but also as solvent. A comparison of the data in Table III with those in Table II indicate that the principal effect of the large excess of ammonia is operative in the liquid condensate in trap I rather than in the gaseous reaction tube. We believe, therefore, that the excess of ammonia functions as a diluent for the chloroamine, hydrazine, and ammonium ion. According to this hypothesis,

we should not be surprised that in the anhydrous system an even higher ammonia to chlorine ratio is required for a good yield of hydrazine than in the aqueous Raschig synthesis.

Research toward the more complete understanding of the nature of this reaction and toward the improvement of the yield of hydrazine is being continued in this laboratory.

Flame Propagation. IV. Correlation of Maximum Fundamental Flame Velocity with Hydrocarbon Structure

BY R. R. HIBBARD AND B. PINKEL

A correlation has been developed between the maximum fundamental flame velocity of hydrocarbons burning in air and the structure of the hydrocarbon. This maximum velocity appears to be a function of the concentrations of the various types of carbon–hydrogen bonds in the inflammable mixture. Maximum flame velocities can be calculated from an equation of the type: flame velocity $= N_A K_A + N_B K_C + N_C K_C \ldots$ where N_A, N_B, $N_C \ldots$ are the concentrations of the various types of C–H bonds and K_A, K_B, $K_C \ldots$ are empirically derived flame speed coefficients. Maximum flame velocities have been calculated for 34 hydrocarbons and compared with experimentally observed values. The average difference between calculated and observed flame velocity is less than 2% if one hydrocarbon is omitted from the average and the derived coefficients line up in approximately the order expected from other chemical considerations.

Introduction

A study has been made of the flame speed data of Gerstein, Levine and Wong[1] in an attempt to determine what elements of hydrocarbon structure might account for the observed variations in flame speed. It was hoped that some relationship could be established between flame speed and structure which would permit the estimation of flame speeds for any hydrocarbon and eliminate the necessity for the experimental determination of this property.

Preliminary work showed little promise in attempts to correlate the concentrations of the various types of carbon–carbon bonds with maximum fundamental flame velocity (U_f). However, it was found that a reasonably accurate prediction of U_f could be made on the basis of the concentrations of the various types of carbon–hydrogen bonds in the hydrocarbon molecule. An empirical equation is proposed which gives U_f as a function of the concentrations of the various types of C–H bonds and parameters expressing the contribution of each type of C–H bond to U_f.

The values for these flame speed parameters are determined from the experimental data of Gerstein, et al. The equation is then used to calculate U_f for 34 hydrocarbons and a comparison is made of the calculated and experimental values. While it appears that the rate of burning can be predicted from the concentrations of the various types of C–H bonds, no attempt is made, herein, to propose an oxidation mechanism and the results are presented on an empirical basis only.

(1) M. Gerstein, O. Levine and E. L. Wong, THIS JOURNAL, **73**, 418 (1951).

Analysis

It was assumed, in this study, that U_f was dependent on all of the various types of C–H bonds in the hydrocarbon molecule and that each of these types had associated with it a different flame speed coefficient which represented the contribution of this type bond to the net flame speed. The simplest equation which would represent the contribution of each type of C–H bond to U_f is an additive function of the product of the concentration of each type of bond times the corresponding flame speed coefficient, such as

$$U_f = N_A K_A + N_B K_B + N_C K_C \ldots \qquad (1)$$

where N_A, N_B, $N_C\ldots$ are the numbers of the various types of C–H bonds per unit volume of hydrocarbon–air mixture, and K_A, K_B, $K_C,\ldots$, are the flame speed coefficients of these bonds.

Equation (1) assumes that the contribution of each type of C–H bond to U_f is not influenced by other bonding effects in the carbon skeleton of the hydrocarbon. While this appears to be true as a first approximation for alkanes and alkenes, there appears to be a considerable effect by the alkyne $C\equiv C$ bond on these C–H bonds which are on carbon atoms situated alpha to the $C\equiv C$. This effect is introduced into the equation by means of a factor, M, which introduces terms which augment the contribution of those C–H bonds which are on carbon atoms placed alpha to the $C\equiv C$ bond. The equation then is modified to read

$$U_f = N_A K_A + N_B K_B + N_C K_C \ldots + M N_{B\alpha} K_B + M N_{C\alpha} K_C \qquad (2)$$

where M is the activation factor for alpha placed