

Short Communication

A new priority sequence rule for the theoretical determination of products of explosion reactions

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A new priority sequence rule for the theoretical prediction of products of explosion reactions is derived from the standard enthalpies of formation of the products using the gaseous states of the relevant elements. The standard enthalpies were calculated and arranged in increasing order to form a priority sequence rule of products in the order H₂O, CO, CO₂, based on the fact that a compound with lower enthalpy is more readily formed than the one with higher enthalpy and with this sequence rule, the products of incomplete explosions were predicted. The predicted products should be close to the actual explosion products as the data used are those that fitted the conditions of the explosion. The procedure is devoid of discrepancy that would warrant modification of the sequence rule as seen to be inherent in the current rule in use. The new *sequence* rule is simple, with no calculations and should replace the one hitherto in use.

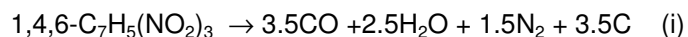
Key words: Theoretical explosion products, new theoretical sequence rule.

INTRODUCTION

Many organic combustion reactions utilizing external oxygen can be made to burn completely, the products of the reaction easily determined and the balanced equation of reaction written. Some organic compounds especially the explosives called CHNO explosives are rich in intrinsic oxygen in combination and which may be sufficient for complete combustion or not. Explosives on slight percussion go off releasing tremendous energy and large volume of gaseous products under high pressure within a split second. Products of explosion can be experimentally determined but results from such experiments have been reported (Bailey and Murray, 1998) to vary with experimental conditions and the loading density of the test vessel. This results to variability in explosion products and balanced equation of reaction.

The thermodynamic and thermo-chemical calculations with any combustion reaction rely on the balanced equation of the combustion and the heat output. For any explosive, the effectiveness is determined through the measurement of performance parameters as heat, temperature, pressure etc of the explosion. The absolute values of the parameters could be determined through painstaking experimentation but for comparison of explosives, theoretical values are preferred as experimental procedures are tedious. The theoretical values of the

parameters still need balanced equation of reaction. Kistiakowsky and Wilson (Bailey and Murray, 1998), developed certain rules based on Ω (the percentage by weight of oxygen, positive or negative, remaining after the explosion assuming that all the carbon and hydrogen have been converted to CO₂ and H₂O) to enable one write the theoretical products. The rules give priority sequence of products as CO, H₂O, CO₂ with nitrogen always appearing as N₂ for CHNO explosives. Others modified the sequence rule to H₂O, CO for explosives with Ω between -10 and up to -40. The variations in experimental products and the application of the varied rules result to some authors (Bailey and Murray, 1998; Bahl and Bahl, 2006; Sharmer, 2006) reporting the theoretical balanced equation of explosion of trinitrotoluene as:



Coupled with the variations in the sequence rules is that the calculation of Ω is lengthy. These problems associa-

Table 1. ΔH° (kJ mol⁻¹) of formation of hydrogen and carbon species.

Atomization*	Formation**
H ₂ (g) → 2H(g) $\Delta H^\circ = 432.2$	H ₂ (g) + 0.5O ₂ (g) → H ₂ O(g) $\Delta H^\circ = -241.8$
C(s) → C(g) $\Delta H^\circ = 713.6$	C(s) + 0.5O ₂ (g) → CO(g) $\Delta H^\circ = -110.5$
O ₂ (g) → 2O(g) $\Delta H^\circ = 493.3$	C(s) + O ₂ (g) → CO ₂ (g) $\Delta H^\circ = -393.4$

s = solid, l = liquid, g = gas, *Brown, (1972). **Robert and Farington (1980).

ted with the rule based on Ω initiated the search for a suitable criteria for use in generating a priority sequence rule that is simple in manipulation, applicable (without amendment) to the wide range of CHNO explosives and will give theoretical products very close to the observed one.

METHODOLOGY

Use of enthalpy in the derivation of the priority sequence rule

The basic assumption pertaining to the explosion products of any CHNO explosive deficient in intrinsic oxygen is that carbon burns to any one or combination of CO, CO₂, and C and hydrogen to either H₂O and or H₂, nitrogen turns out always as N₂. In a CHNO explosive, it is only carbon and hydrogen that utilise the intrinsic oxygen. For a CHNO explosive, with insufficient intrinsic oxygen, the carbon and hydrogen content will compete for the available oxygen. Which product, CO or CO₂ or H₂O is first formed will depend on which has lower activation energy (ΔE_a). The rate of reaction is actually governed by (ΔE_a), (Morrison and Boyd, 2001) and under the same conditions; reactions with lower ΔE_a go faster than those with high ΔE_a . Unfortunately ΔE_a of many reactions, of which the reactions making up explosions are part of, are unavailable for use in comparing the ease of formation of products of explosions. In this circumstance ΔH° forms a good substitute and can be utilized for the above gradation.

When ΔH° values in Table 1 are used for the calculation under this condition, the results show values of H₂O (-1177.3), CO (-1317.4), CO₂ (-1600.3) kJ mol⁻¹, suggesting a prioritisation sequence of H₂O, CO, CO₂. With this priority sequence, explosion products are written for each explosion in Table 2, which also contains the products from the application of Ω rule.

RESULTS AND DISCUSSION

The explosion products predicted by Ω sequence rule and the new sequence rule are tabulated in Table 2. Table 2 shows the same products predicted by the two rules up to $\Omega = -22$ with variation setting in after this value. For $\Omega = -32$ to -48 , the products contain H₂ in place of C predicted by the new sequence rule and for $\Omega = -61$ to -75 , Ω sequence rule predicts C and H₂ while the new sequence rule predicts C as the un-oxidised elements.

In general the Ω sequence rule portrays the majority of the explosives as exploding neatly that is, without soot or carbon but it is known that most explosives are mixed to make them more effective and smokeless. Table 2 also

shows that with Ω lower than -22 , the carbon and hydrogen products no longer follow definite sequence, e.g. EDNA ($\Omega = -32$) has products CO + H₂O + H₂ (like other explosives with Ω less than -32 but PENTHRYL ($\Omega = -35$) has CO + H₂O. These discrepancies are not observed in the products predicted by the new rule.

Although the reason for the product sequence CO, H₂O, CO₂ and C is not given, the rational must have been guided by the enthalpies (ΔH° in kJ mol⁻¹) of formation of CO (g) (-110.5); H₂O (g) (-241.8) and CO₂ (g) (-393.4) from the elements in their native states, and reactions such as H₂O (g) + C (g) → CO (g) + H₂ and C (g) + CO₂ (g) → CO (g) also taking place. Such reactions as above are insignificant as shown by the presence of much soot accompanying the explosion of single substance explosives with Ω less than -10 and this necessitated the practice of compounding explosives as mixtures.

Prioritisation of explosion products by the enthalpies (ΔH° in kJ mol⁻¹) of formation of CO (g) (-110.5); H₂O (g) (-241.8) and CO₂ (g) (-393.4) from the elements in their native states, is also incorrect because it is accepted that the mechanism of explosions is not fully understood and that during explosion, the explosive fragments to chemical species that recombine to form the products. The enthalpy of formation (ΔH°) of the gaseous products should thus be calculated from the gaseous atomic states from which the products are formed and the estimation of the parameters of any explosive should utilize the balanced equation at the moment of fragmentation and recombination of the chemical species.

From Table 2, the two methods gave the same total number of moles of products but not the same total volume of products because by the new method, carbon at the instant of and immediately after explosion is in gaseous state. By the new procedure, the whole system at the time of explosion could be viewed as being in a state of "plasma" in which all the particle present contribute to the total volume and total pressure and the energy output being that lost by the "plasma" after the explosion. In the calculation of total volume, the volume of carbon (regarded as solid) is neglected by the rule in vogue but by the new rule, it is not disregarded as it is in gaseous state. Temperature calculations utilise the molar specific heats of the products. Temperature values obtained will be almost the same using the set of the products from any of the sequence rules except in cases

Table 2. Comparison of theoretical products derived from Ω and the new Sequence rule for CHNO explosives.

Explosive Name/Formula	Ω Value	Theoretical Explosion Products less N_2	
		Ω Sequence Rule	New Sequence Rule
Nitro-glycerine $C_3H_5N_3O_9$	4.0	$3CO_2, 2.5H_2O, 0.25O_2$	Same
EDGN, $C_2H_4N_2O_6$	0	$2CO_2, 2H_2O$	Same
PETN, $C_5H_8N_4O_{12}$	-10	$2CO, 4H_2O, 3CO_2$	Same
RDX, $C_3H_6N_6O_6$	-22	$3CO, 3H_2O$	Same
HMX, $C_4H_8N_8O_8$	-22	$4CO, 4H_2O$	Same
EDNA, $C_2H_6N_4O_4$	-32	$2CO, 2H_2O, H_2$	$CO, 3H_2O, C$
PENTRYL, $C_8H_6N_6O_{11}$	-35	$8CO, 3H_2O$	Same
Picric acid $C_6H_3N_3O_7$	-46	$6CO, H_2O, 0.5H_2$	$5.5CO, 1.5H_2O, 0.5C$
TETRYL, $C_7H_5N_5O_8$	-47	$7CO, H_2O, 1.5H_2$	$5.5CO, 2.5H_2O, 1.5C$
Nitrocellulose $C_6H_7N_3O_8$	-48	$6CO, 2H_2O, 1.5H_2$	$4.5CO, 3.5H_2O, 1.5C$
HEXYL, $C_{12}H_5N_7O_{12}$	-53	$12CO, 2.5H_2$	$9.5CO, 2.5H_2O, 2.5C$
TNB, $C_6H_3N_3O_6$	-56	$6CO, 1.5H_2$	$4.5CO, 1.5H_2O, 1.5C$
DINOL, $C_6H_2N_4O_3$	-61	$5CO, H_2, C$	$4CO, H_2O, 2C$
TNT, $C_7H_5N_3O_6$	-75	$6CO, 2.5H_2, C$	$3.5CO, 2.5H_2O, 3.5C$

where hydrogen substitutes carbon in the products from Ω process. This is so because gaseous hydrogen and gaseous carbon have almost the same molar heat but solid carbon (in Ω process) has very lower molar heat compared to gaseous carbon, in such situations, the new procedure gives slightly higher temperature. It could also be that the presence of hydrogen in the sequence rule in vogue is to boost the temperature to near the observed one; the presence of gaseous carbon takes care of this. Although the predicted theoretical products are approximate and are for use in comparing the effectiveness of explosives the products predicted should be closer to the actual ones observed for single explosive materials. The new procedure uses the appropriate reaction conditions with the appropriate principle for the situation and so is reliable. The application of the new method to mixed explosives will follow the same principles for each component of the mixture.

Conclusion

The products sequence H_2O , CO , CO_2 predicted from the new rule are based on the appropriate reaction conditions, chemical and thermo-chemical principles and hence reliable and should replace the existing Ω process.

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