THE RELATIONSHIP BETWEEN PERFORMANCE AND CONSTITUTION OF PURE ORGANIC EXPLOSIVE COMPOUNDS

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I. INTRODUCTION

An intriguing problem of structural organic chemistry which has not been reviewed in the published literature is the relationship between the performance of pure explosive compounds and their constitution. Early attempts at developing a theory for predicting the power of explosive compounds have been almost entirely based on thermodynamic concepts. Berthelot (1) wrote one of the earliest and best expositions on this subject, but the relationship between chemical structure and performance was not considered, since publication was prior to most of the work in structural organic chemistry. Brunswig (4), Moser (11), Marshall (10), Stettbacher (22), and others (6, 13) have examined this field of chemistry in much the same manner as Berthelot.

Some investigators (3, 10, 18, 22) have implied the value of oxygen balance, a property which can be calculated from empirical formulas, but none has stressed its fundamental applicability. Although the idea has been implicit in the thinking of those familiar with the field, there are few documented publications of it aside from a study of dynamites (14) and one by Roth (20) on mixtures of tetranitromethane and nitrobenzene or nitroglycerin.

A single effort to develop a relationship between performance and structural composition has been made. This is that of Pletz (15), who proposed a theory of "explosophores" and "auxoexploses," analogous to the Witt theory of chromophores and auxochromes and to the Ehrlich theory of toxophores and autotoxes. According to this theory the explosive properties of any given substance depend upon the presence of definite structural groupings, called explosophores. the auxoexploses fortify or modify the explosive properties brought about by the explosophore.

On the basis of this theory Pletz examined eleven classes of organic compounds and subdivided all explosives into eight classes containing as "explosophores":

I. —NO_2 and —ONO_2 groups connected to organic or inorganic radicals (for example, HNO_3, $C(NO_2)_4$, and $C_6H_3(NO_2)_3$).

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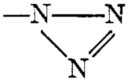
[1] The authors are greatly indebted to Colonel C. H. M. Roberts and Dr. L. R. Littleton of the Office of the Chief of Ordnance for assistance and encouragement in connection with the initiation and progress of the investigation, and to many others expert in the field who have given freely of their time and knowledge. The work was done under Contract W-19-020-ORD-6436 with the Office of the Chief of Ordnance and has been released by the War Department for publication.

II. $-N{=}N-$ and  $\underset{\mathrm{N}}{-\mathrm{N}\text{——}\mathrm{N}}$ groups, connected to inorganic or organic radicals (for example, PbN_6 and CH_3N_3).

III. $-NX_2$ group (for example, NCl_3 and $RNCl_2$).

IV. $C{=}N-$ group (for example, HONC and $Hg(ONC)_2$).

V. $-OClO_2$ and $-OClO_3$ groups, connected to inorganic or organic radicals (for example, $KClO_3$, $KClO_4$, and certain organic perchlorates).

VI. —O—O— and —O—O—O— groups connected to inorganic or organic radicals (for example, peroxides and ozonides).

VII. $-C{\equiv}C-$ group (for example, acetylene or its metallic derivatives).

VIII. A metal atom connected by an unstable bond to the carbon of certain organic radicals (for example, organic compounds of mercury, thallium, and lead).

While the arrangement of Pletz embraces the whole explosive field in a purely empirical fashion, the distinction between the terms "explosophore" and "auxoexplose" is vague, poorly developed, and of little practical usefulness.

He and other authors were not fortunate in having before them full information on a great variety of explosive compounds, for, although a considerable body of data had been amassed by workers throughout the world prior to the Second World War, a large fraction of it was buried in confidential government or industry files. That which was published appeared in relatively obscure journals and was not infrequently of questionable authenticity. Before any study such as the one to be described here could be undertaken, it was necessary that this information be assembled in usable form. This tremendous task was the subject of an extremely successful wartime project conducted by Dr. A. H. Blatt. It can be said without qualification that his compilation alone has made possible the presently reported treatment.

The object of the work has been the collation and classification of information through relationships which exist between organic structure and the explosive properties of greatest interest in military applications. These properties have been judged to be power (the work capability or strength of an explosive) and brisance (the shattering effect connected with the speed of detonation). Other properties are also mentioned briefly. The compounds considered are chiefly "high explosives," as contrasted with initiating explosives and commercial compositions.

Physical chemistry, by the use of standard thermodynamic concepts, has successfully treated the subject quantitatively through the additivity of bond energies and the use of standard calorimetry. This aspect is touched on lightly here, for it is hoped that it may someday be published fully by those who have been so successful with it.

It is believed that using the concepts explained one should be better guided in the synthesis of new and powerful high explosives and the prediction of their explosive properties. Whether any compound would thereby be discovered greatly superior to the excellent explosives now in use is problematical. For military purposes, moreover, it is likely that items other than explosive performance would be governing, such as economics, effectiveness in special uses, and difficulty of synthesis.

II. CONSTITUTION AND EXPLOSIVE POWER

An explosive compound can be looked upon as a chemical combination of atoms in a metastable state which spontaneously, on passage of a detonating wave, rearrange themselves to give simple products with a concurrent liberation of large volumes of gas and considerable energy, mainly in the form of heat. For purposes of this treatment the detonation products may be considered as consisting of the free elements or their several oxides. They are chiefly water, carbon or its oxides, and nitrogen, although traces of other substances are also known to be formed, such as hydrogen cyanide and methane. Other elements are occasionally encountered, such as chlorine, sulfur, lead, or mercury, but organic high explosives in the main are composed of combinations of only four elements: carbon, hydrogen, oxygen, and nitrogen.

Since combustion is the process taking place, a simple computable term should be of value in stating the degree to which oxidation is possible. For this purpose the expression known as *oxygen balance* is useful. This is given as the percentage of oxygen required for complete conversion of the carbon and hydrogen present to carbon dioxide and water. For any compound containing x atoms of carbon, y atoms of hydrogen, and z atoms of oxygen, the oxygen balance = $\left[-1600\left(2x + \frac{y}{2} - z\right)\right]\Big/$molecular weight. Thus an explosive having perfect balance to yield carbon dioxide and water has zero balance, one lacking sufficient oxygen has a negative balance, and one containing excess oxygen has a positive balance. It is noted that with very few exceptions explosives are of decidedly negative balance. This method of computation makes no distinction between oxygen already bound to carbon or hydrogen and that bound to nitrogen. The latter might be termed "effective" oxygen and differs from the former in that it is loosely held and available for subsequent combustion.

A term which will describe power quantitatively is more difficult to devise, although it has been successfully accomplished by unpublished thermodynamic treatment. Two of the most commonly employed experimental tests designed for power measurement are the so-called Trauzl lead block expansion test (12, 16, 25) and the ballistic mortar test (24). The former is a classical method and depends on determining the expansion caused in a block of "pure" lead when a standard weight of explosive is detonated in a specified cavity under controlled confinement. It is customarily expressed in this country in terms of TNT, whose arbitrary value is given as 100. Whether the lead block test is a measure of power alone or of an uncertain combination of power and brisance is a subject of contention but not of great importance, since it can be shown that power and brisance appear to vary concomitantly. Caution should govern the use of the lead block values, however, as an absolute measure of power.

The second method of testing for power is by the ballistic mortar, in which a standard explosive charge is fired in a heavy pendulum mortar and the angle of recoil is measured. This method can also be related to TNT as a standard of 100, and is considered to be uncomplicated by brisance. It is probably safer to use ballistic mortar values in direct comparisons of explosive power, for "the high explosive instead of being caused to do work against a varying and unknown resistance as in the lead block is fired in a suitable type of gun, so that the work done by expansion of the products of detonation is measured in absolute mechanical units" (26).

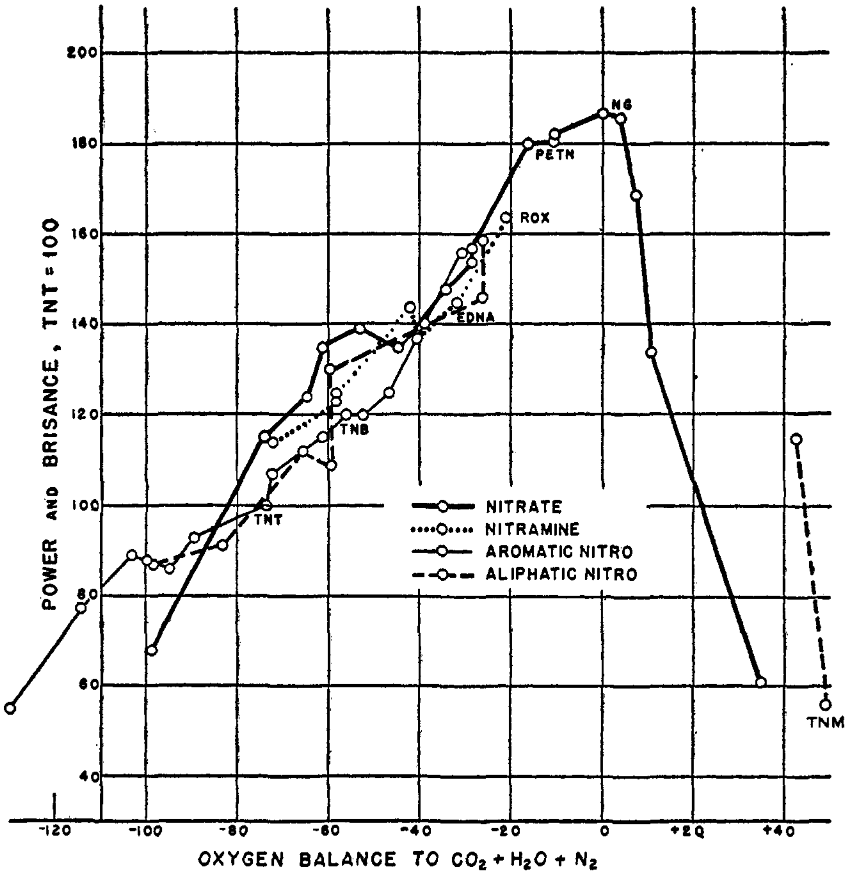


FIG. 1. Effect of oxygen balance on power and brisance of explosives compared with TNT in the lead block expansion test. Primary plosophores.

The results of both methods appear to be equally useful and to yield the same conclusions. The lead block data, however, are much more extensive.

If one plots the lead block values for known organic explosives against their indicated oxygen balance, one is confronted with a mass of points scattered at random over the whole graph. This apparent confusion can be very quickly resolved by the use of the term *plosophore*.[2] By analogy with color chemistry, this has been defined as a group of atoms which on substitution into a hydrocarbon is capable of forming an explosive compound. Inspection of the substituent groups which can function in this way indicates at once that there are two classes of plosophores, differing sharply in effectiveness and consistency in producing power and hence properly called *primary* and *secondary*.

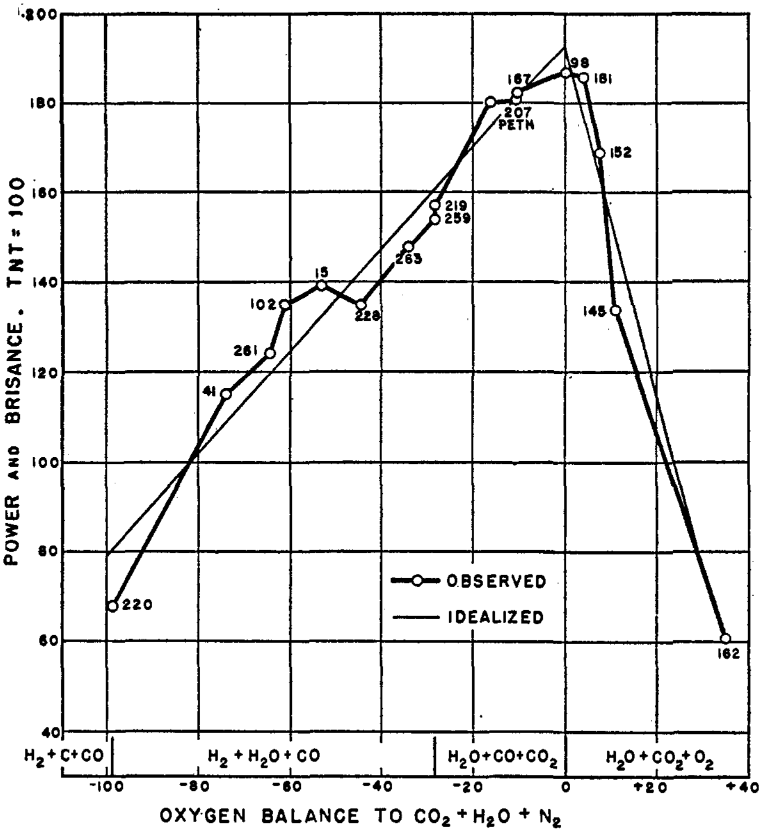


FIG. 2. Effect of oxygen balance on power and brisance of explosives compared with TNT in the lead block expansion test. Primary plosophores: nitrate.

Primary phosophores include the following groups: nitrate ester, aromatic nitro, aliphatic nitro, and nitramine. The secondary plosophores make up the remainder and include such groups as azo, azide, nitroso, peroxide, ozonide, perchlorate, etc.

In figure 1[3] all compounds containing carbon, hydrogen, and any one type of

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[2] The present terms were derived independently of Pletz (15). Since their definition and use differ from his terms, a different nomenclature is felt to be justified.

[3] The abbreviations on figure 1 for the more important high explosives stand for the scientific names as follows: TNT = 2,4,6-trinitrotoluene; TNB = 1,3,5-trinitrobenzene; TNM = tetranitromethane; RDX = cyclotrimethylenetrinitramine; PETN = pentaerythritol tetranitrate; NG = nitroglycerin; EDNA = ethylenedinitramine.

the four primary plosophores are compared in lead block value and oxygen balance. Considering that all the data available have been used without regard to quality of source and that some of them have been interpolated from ballistic mortar results by the use of calculated factors, the family of curves which results is remarkably consistent. The conclusion is inescapable that power is directly related to oxygen balance for primary plosophoric compounds, that it is at a maximum in compounds whose balance is close to zero, and that the four types of explosives are roughly equal to each other at given balance although their indicated maxima may not exactly coincide (3, 14).

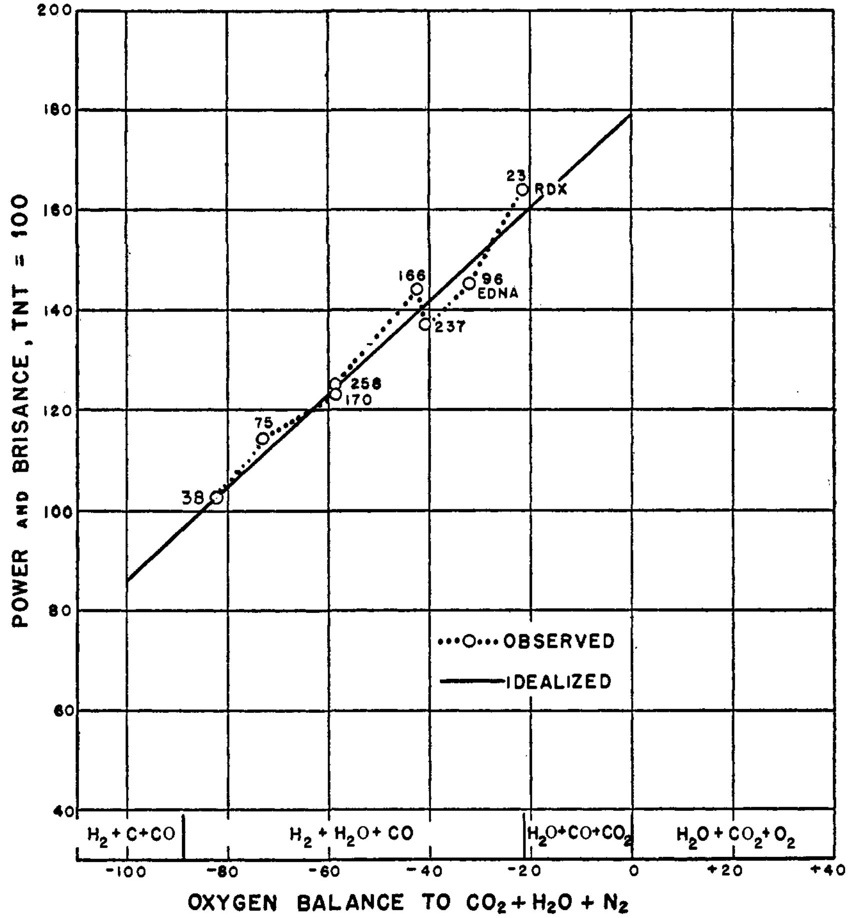

FIG. 3. Effect of oxygen balance on power and brisance of explosives compared with TNT in the lead block expansion test. Primary plosophores: nitramine.

Treatment of each plosophoric series separately and use of the least square method for the derivation of idealized straight lines to express the data yield the results plotted in figures 2 to 5. It is noted that these lines do not coincide, owing to a real difference or the inadequacy of the data. In these and other figures the data have been conveniently summarized by the drawing of idealized curves. The authors consider them as useful generalizations of no great accuracy. When straight lines are drawn they are shown to reach a maximum at zero oxygen balance, but in practice it appears likely that the true maximum will be found in the region of negative balance, although close to zero. Because of the scant data in this region, it is impossible to locate the point exactly. The

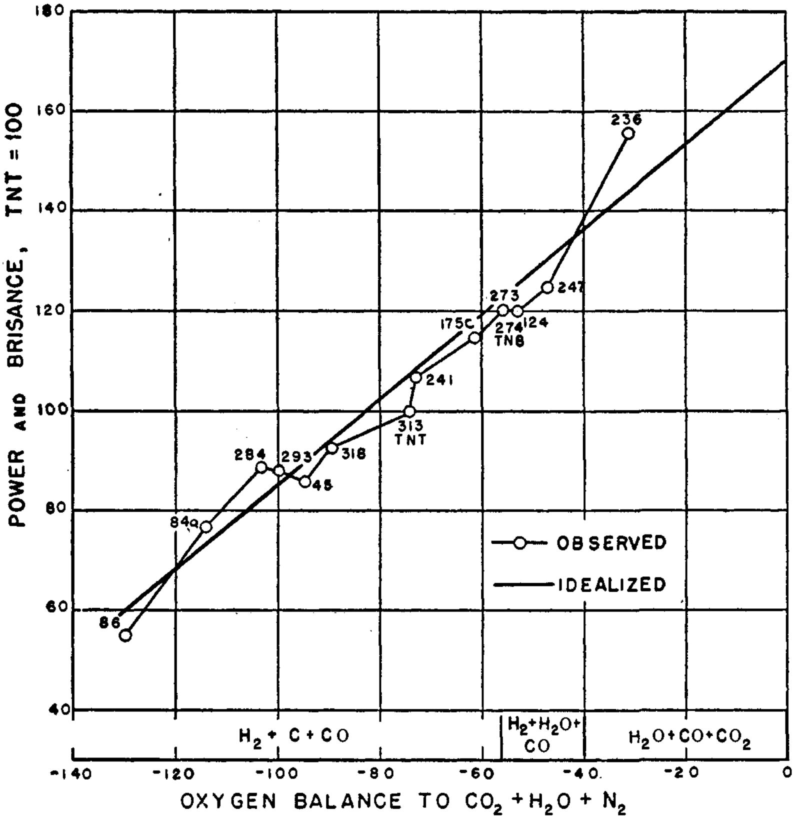

FIG. 4. Effect of oxygen balance on power and brisance of explosives compared with TNT in the lead block expansion test. Primary plosophores: aromatic nitro.

figures also bear numbers which refer to the individual compounds listed in table 1. Some unidentified points are reported where release of information could not be secured. It is observed at once that only the nitrate ester series is reasonably complete, with the other three series lacking examples in the interesting region of oxygen balance lying between −20 per cent and ±0 per cent. At the foot of figures 2 to 5 are approximate indications of the assumed products of detonation as they vary with oxygen balance.

Having established the desirability of primary plosophores as power-producing groups, it is of interest to learn whether the presence in a single molecule of more than one type of such groups has an effect. Such molecules may be termed *hybrid*.

Of the six possible hybrids of two primary plosophores, four are represented by available data; in addition, examples of molecules are found containing three different primary plosophores. All these hybrids are given in figure 6, together with the single idealized line for the performance of the pure primary plosophores. It is interesting to note how abruptly the data dwindle in passing beyond an oxygen balance of −20 per cent, thus duplicating the situation already noted in figure 1. Nevertheless, the result is obvious: hybrids are the equivalent of pure types, although they tend to exhibit somewhat greater variability. In any synthetic program on high explosives this equivalence of hybrids will be of importance, because it extends enormously the synthetic possibilities.

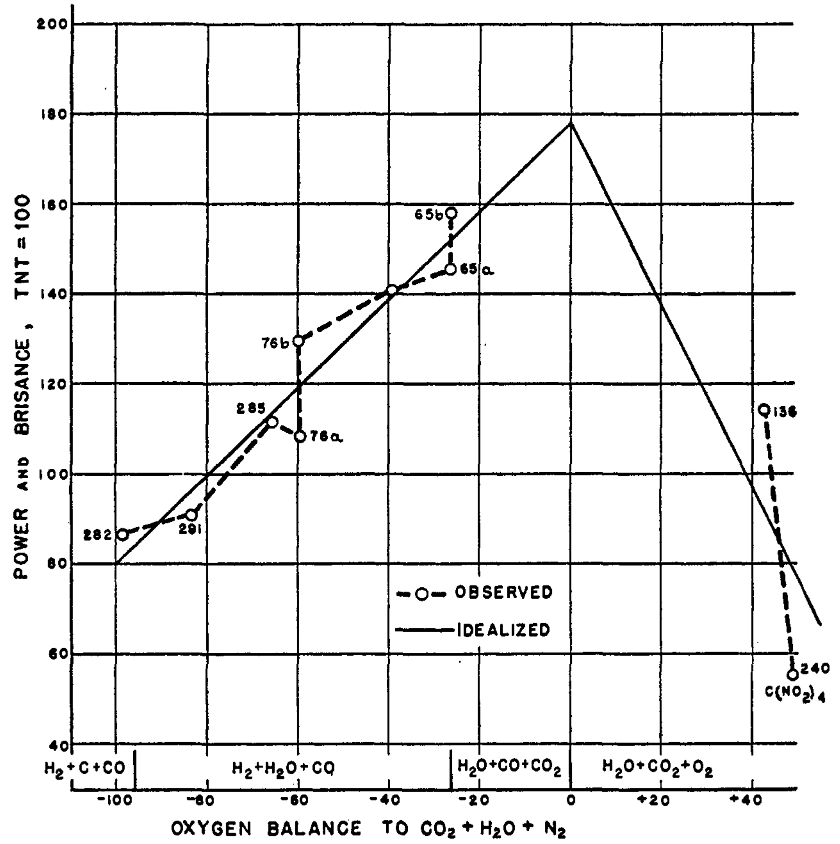

FIG. 5. Effect of oxygen balance on power and brisance of explosives compared with TNT in the lead block expansion test. Primary plosophores: aliphatic nitro.

The very clean-cut relationship between power and oxygen balance vanishes

TABLE 1
Index of compounds

COMPOUND NUMBER	NAME
3	Ammonium nitrate
5	Ammonium picrate
9	Azidoethyl alcohol
10	Azidoethyl nitrate
15	1,3-Butylene glycol dinitrate
17	β-Chloroethyl nitrate
18	Cyanoethyl nitrate
20	Cyanuric triazide
23	Cyclotrimethylenetrinitramine
24	Cyclotrimethylenetrinitrosamine
28	Diazodinitrophenol
32a	1,2-Dichloro-3,5-dinitrobenzene
32b	1,3-Dichloro-4,6-dinitrobenzene
33	Dicyandiamidine perchlorate
34	Di(β,γ-dihydroxypropyl)oxamide tetranitrate
37	Diethylene glycol dinitrate
38	*N*,*N'*-Dimethyl-*N*,*N'*-dinitroethylenediamine
41	2,2-Dimethylpropane-1,3-diol dinitrate
43	2,4-Dinitroaniline
44	2,4-Dinitroanisole
45	*m*-Dinitrobenzene
46	2,4-Dinitrobenzyl nitrate
50	Dinitrodiethyloxamide
51	1,4-Dinitro-3,6-diketopiperazine
52	2,3-Dinitro-2,3-dimethylbutane
53	1,4-Dinitro-2,5-dimethyl-3,6-diketopiperazine
57	1,4-Dinitro-2,5-dimethylolbenzene dinitrate
58	*N*,*N'*-Dinitrodimethyloxamide
59	1,3-Dinitro-2,2-dimethylpropane
60	Dinitrodimethylsulfamide
62	1,3-Dinitro-4,5-dinitrosobenzene
64	Dinitrodi(β-nitroxyethyl)sulfamide
65a	1,1-Dinitroethane
65b	1,2-Dinitroethane
66	*N*,*N'*-Dinitroethyleneurea
67	2,5-Dinitrofuran
71	2,4-Dinitrophenol
72	β-(2,4-Dinitro)phenoxyethyl nitrate
73	3,5-Dinitrophenylnitromethane
74	2-(3',5'-Dinitrophenyl)-2-nitro-1,3-propanediol dinitrate
75	1,4-Dinitropiperazine
76a	1,1-Dinitropropane
76b	2,2-Dinitropropane
80	2,4-Dinitrosoresorcinol
81	1,4-Dinitro-1,1,4,4-tetramethylolbutane tetranitrate

TABLE 1—*Continued*

COMPOUND NUMBER	NAME
82	1,5-Dinitro-1,1,5,5-tetramethylolpentane tetranitrate
84a	2,4-Dinitrotoluene
84b	2,6-Dinitrotoluene
86	4,6-Dinitro-*m*-xylene
89	Dipentaerythritol hexanitrate
93	Erythritol tetranitrate
94	Ethanolamine dinitrate
95	Ethylenediamine dinitrate
96	Ethylenedinitramine
98	Ethylene glycol dinitrate
102	Ethyl nitrate
105	Glycerol 1,2-dinitrate
107	Glycerol α-2,4-dinitrophenyl ether dinitrate
108	Glycerol α,α′-hexanitrodiphenyl ether β-nitrate
109	Glycerol monochlorohydrin dinitrate
111	Glycerol monolactate trinitrate
112	Glycerol α-monomethyl ether dinitrate
113	Glycerol α-2,4,6-trinitrophenyl ether dinitrate
114	Guanidine nitrate
115	Guanidine perchlorate
116	Guanylnitrourea
118	Hexamethylenetriperoxidediamine
120	Hexamine dinitrate
123	Hexanitroazobenzene
124	Hexanitrobiphenyl
125	Hexanitrodiphenylamine
127	β-(Hexanitrodiphenylamino)ethyl nitrate
128	2,4,6,2′,4′,6′-Hexanitrodiphenyl ether
130	*N*,*N*′-(Hexanitrodiphenyl)ethylenedinitramine
132	Hexanitrodiphenylmethylamine
133	Hexanitrodiphenyl sulfide
134	Hexanitrodiphenyl sulfone
135	Hexanitrodiphenylurea
136	Hexanitroethane
137	Hexanitrohydrazobenzene
138	Hexanitroöxanilide
143	Hydrazine perchlorate
145	Inositol hexanitrate
148	Lactose octanitrate
150	Lead styphnate
151	Maltose octanitrate
152	Mannitol hexanitrate
154	Mercuric fulminate
155	Methazonic acid

TABLE 1—*Continued*

COMPOUND NUMBER	NAME
156	Methylamine nitrate
162	Methyleneglycol dinitrate
163	*N*-Methylethylenedinitramine
166	Methylnitramine
167	Methyl nitrate
168	2-Methyl-2-nitro-1,3-propanediol dinitrate
170	Trimethylene-1,3-dinitramine
172	Pentaerythritol diglycolate tetranitrate
175a	2,4-Dinitrophenylazonitromethane
175b	2,4,6,2′,4′,6′-Hexanitro-3,5,3′,5′-tetrahydroxybiphenyl
175c	Tetranitro-*m*-xylene
178	β-Nitroethanol
181	Nitroglycerin
182	Nitroguanidine
185	Nitromethane
186	1-Nitro-5-methylhydantoin
192	*m*-Nitrophenyldinitromethane
193	Nitrophenylglycol dinitrate
194	1-(*o*-Nitrophenyl)-2-nitroethyl nitrate
197	Nitrosoguanidine
200	Nitrourea
205	Pentaerythritol dimethyl ether dinitrate
206	Pentaerythritol monomethyl ether trinitrate
207	Pentaerythritol tetranitrate
210	Pentanitrodiphenyl ether
212a	Ethyl perchlorate
212b	Ammonium perchlorate
212c	Ethylenediamine diperchlorate
212d	1,2-Propylenediamine diperchlorate
212e	1,3-Propylenediamine diperchlorate
216	Picric acid
217	Picryl chloride
218	Picryl fluoride
219	1,2-Propanediol dinitrate
220	Propyl nitrate
223	Sucrose octanitrate
225	Tetracene (1-guanyl-4-nitrosaminoguanyltetrazene)
228	Tetramethylolcyclohexanol pentanitrate
229	Tetramethylolcyclohexanone tetranitrate
231	Tetramethylolcyclopentanone tetranitrate
233	2,3,4,6-Tetranitroaniline
234	2,3,5,6-Tetranitroanisole
236	1,2,3,5-Tetranitrobenzene
237	Tetranitrodiglycerin
240	Tetranitromethane

TABLE 1—*Concluded*

COMPOUND NUMBER	NAME
241	1,3,6,8-Tetranitronaphthalene
243	2,3,4,6-Tetranitrophenylmethylnitramine
247	2,3,4,6-Tetranitrotoluene
248	Tetra(β-nitroxyethyl)ammonium nitrate
253	Tetryl
258	Trimethylene-1,2-dinitramine
259	Trimethylene glycol dinitrate
261	1,1,1-Trimethylolbutane trinitrate
262	1,1,1-Trimethylol-2-chloroethane trinitrate
263	1,1,1-Trimethylolethane trinitrate
264	Trimethylolnitromethane trinitrate
270	2,4,6-Trinitroaniline
271	2,4,6-Trinitroanisole
272	2,4,6-Trinitrobenzaldehyde
273	1,2,4-Trinitrobenzene
274	1,3,5-Trinitrobenzene
275	2,4,6-Trinitrobenzoic acid
276	2,4,6-Trinitrobenzyl nitrate
277	2,4,6-Trinitro-*m*-cresol
279	2,4,6-Trinitro-1,3-di(methylnitramino)benzene
282	2,2,3-Trinitro-3-ethylpentane
283	Trinitromelamine
284	Trinitromesitylene
285	2,3,3-Trinitro-2-methylbutane
290	2,4,6-Trinitro-3-methylnitraminotoluene
291	2,2,3-Trinitro-3-methylpentane
292	2,4,6-Trinitromonomethylaniline
293	1,3,8-Trinitronaphthalene
294	2,4,6-Trinitrophenetole
295	2,4,6-Trinitrophenoxyethyl nitrate
296	2,4,6-Trinitrophenyl azide
297	2,4,6-Trinitrophenylbutylnitramine
300	2,4,6-Trinitrophenylethylnitramine
305	2,4,6-Trinitrophenyl(1-methylol)propylnitramine nitrate
307	β-(2,4,6-Trinitrophenylnitramino)ethyl nitrate
310	2,4,6-Trinitroresorcinol
313	2,4,6-Trinitrotoluene
314	Trinitrotoluenes
315	2,4,6-Trinitro-1,3,5-triazidobenzene
316	2,4,6-Trinitro-1,3,5-tris(methylnitramino)benzene
318	1,3,6-Trinitro-*m*-xylene
320	Urea nitrate

when one considers secondary plosophores. In figure 7 this is done by comparing the data for these compounds with a single idealized curve for the four primary types obtained by averaging the four separate curves of figures 2 to 5. It is no longer possible to say that increased oxygen balance is accompanied by increased power. This may on occasion be the case, but there is no assurance of it. Further, with few exceptions, secondary plosophores do not significantly exceed primary plosophores as power-producing substituents. Therefore, it can be concluded that secondary plosophores do not recommend themselves as a class in the synthesis of powerful organic explosives. This is not to say that they are useless, for they often impart desirable qualities of another kind as in forming initiating and detonating compounds, but if power and brisance alone are the criteria, the secondary plosophores are to be avoided.

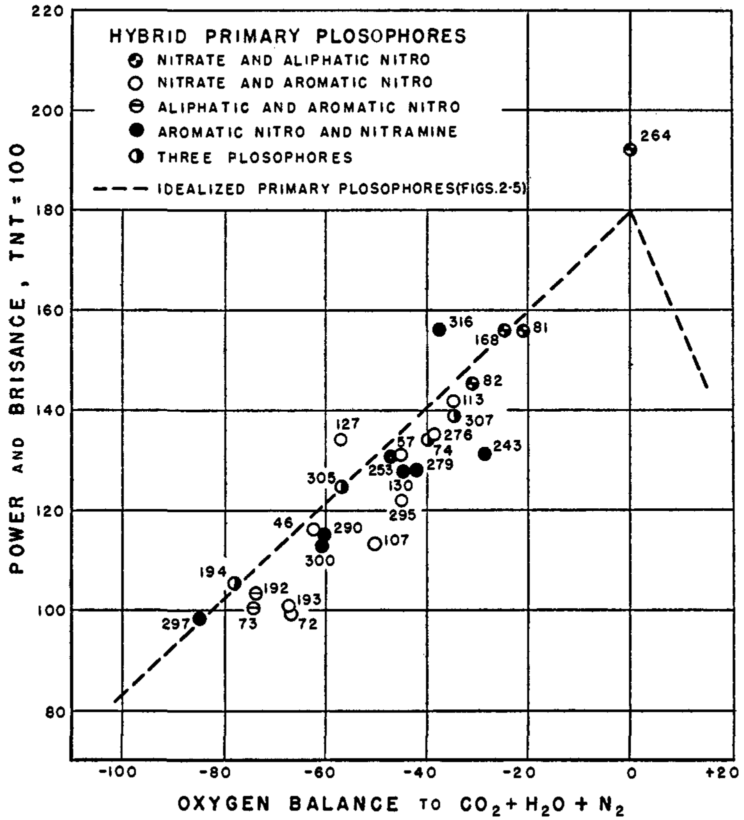

FIG. 6. Effect of oxygen balance on power and brisance of explosives compared with TNT in the lead block expansion test. Hybrid primary plosophoric compounds.

A very common feature of explosives is the presence in them of a large variety of substituent groups which are not plosophoric, since they do not in themselves produce explosive molecules, but which may be expected to alter the explosive properties in the same way that an auxochromic group is found to vary the intensity or shade of a dye. Such substituents may be designated *auxoplosive*.[4] Etymologists may object, because the name implies that such groups will always *aid* the formation of powerful explosives rather than *alter* their performance. Nevertheless, the term is retained in the interests of analogy and it is not believed that any serious confusion will arise. As examples of such groups, one may take hydroxyl, carbonyl, chloride, sulfide, ether, amino, etc. Not infrequently the presence of these groupings affects oxygen balance in a favorable manner, and it is of interest to see whether a concurrent improvement in power is produced. The data in figures 8 and 9 speak for themselves. With hardly an exception auxoplosive groups are shown to be detrimental to power whether or not they appear to improve oxygen balance. This is in agreement with the observation made earlier about "effective" oxygen. It is concluded, therefore, that the chief

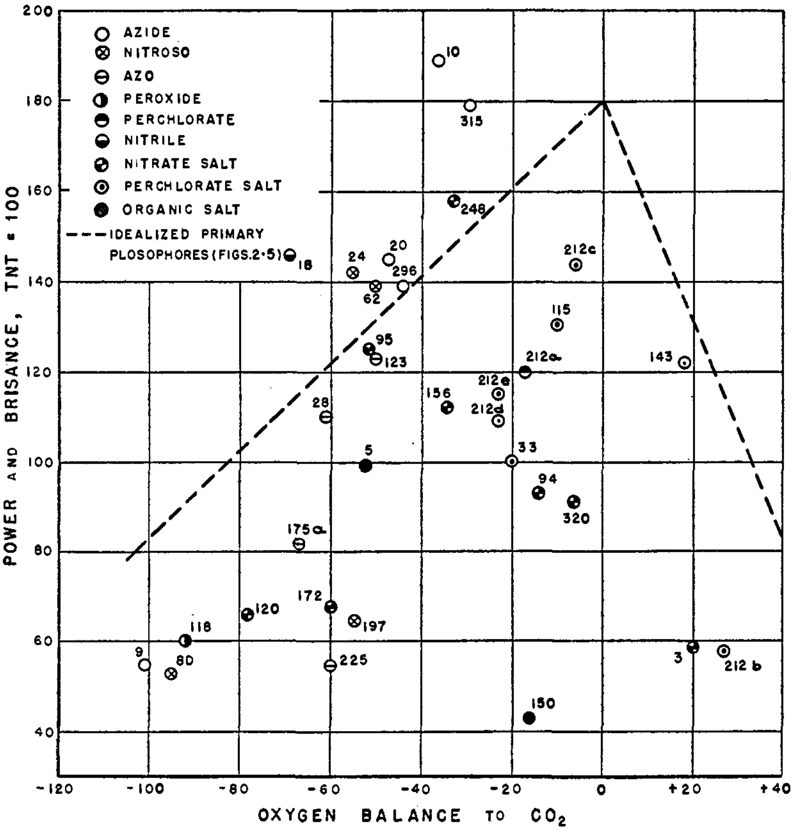

FIG. 7. Effect of oxygen balance on power and brisance of explosives compared with TNT in the lead block expansion test. Secondary plosophores.

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[4] Pletz (15) uses the word "auxoexplose."

justification for the presence of such groups in powerful explosives is expediency in synthesis.

From the above discussion we can now say that power and brisance as measured in the Trauzl lead block are at a maximum for carbon and hydrogen compounds which bear as substituents only primary plosophores and are at or close to zero oxygen balance. The presence of secondary plosophores and auxoplosive groups is not desirable, although on occasion these can be tolerated in the interests of increasing sensitivity (as in initiators) or of synthetic ease. Hybrid molecules may be classed as equivalent to pure plosophoric types.

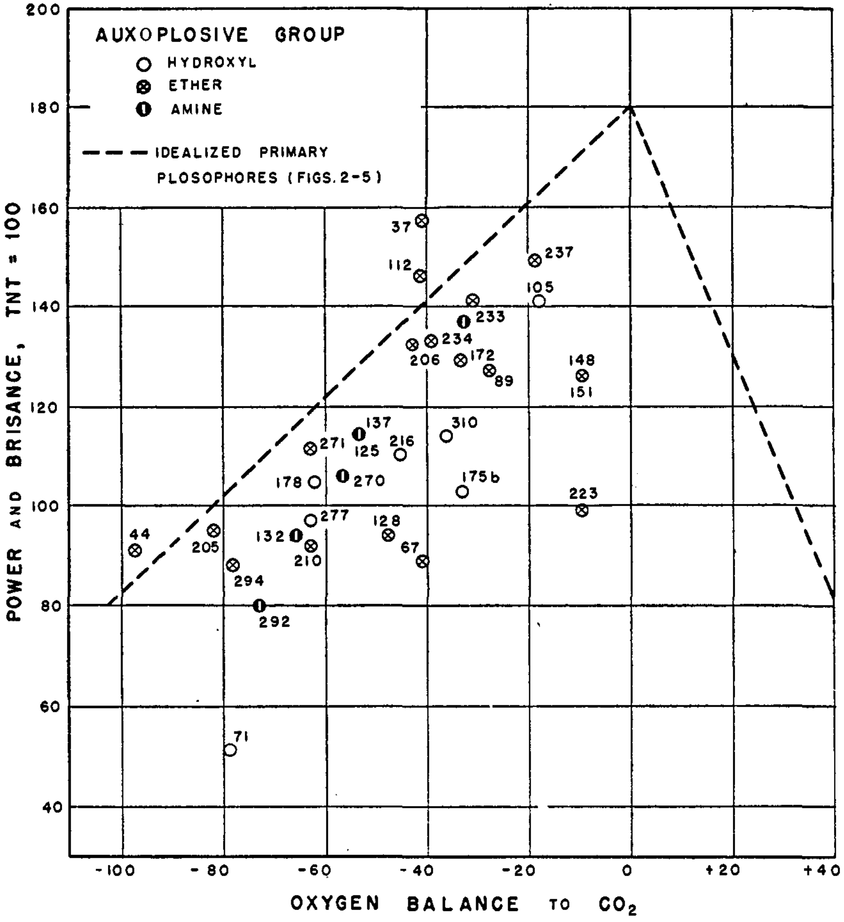


Fig. 8. Effect of auxoplosive groups on power and brisance of primary plosophoric compounds compared with TNT in the lead block expansion test.

Ballistic mortar data yield exactly similar conclusions, as is shown in figures 10 and 11. In these figures it is remarked that the observed power in terms of TNT is usually much lower than in the corresponding lead block graphs. Thus the apparent maximum at the zero balance point is about 160 instead of 180, —a value more comparable to actual experience in use. This points up the earlier recommendation that one should place less significance on an absolute lead block value and should use ballistic mortar results if a comparison of the relative powers of explosives is to be made.

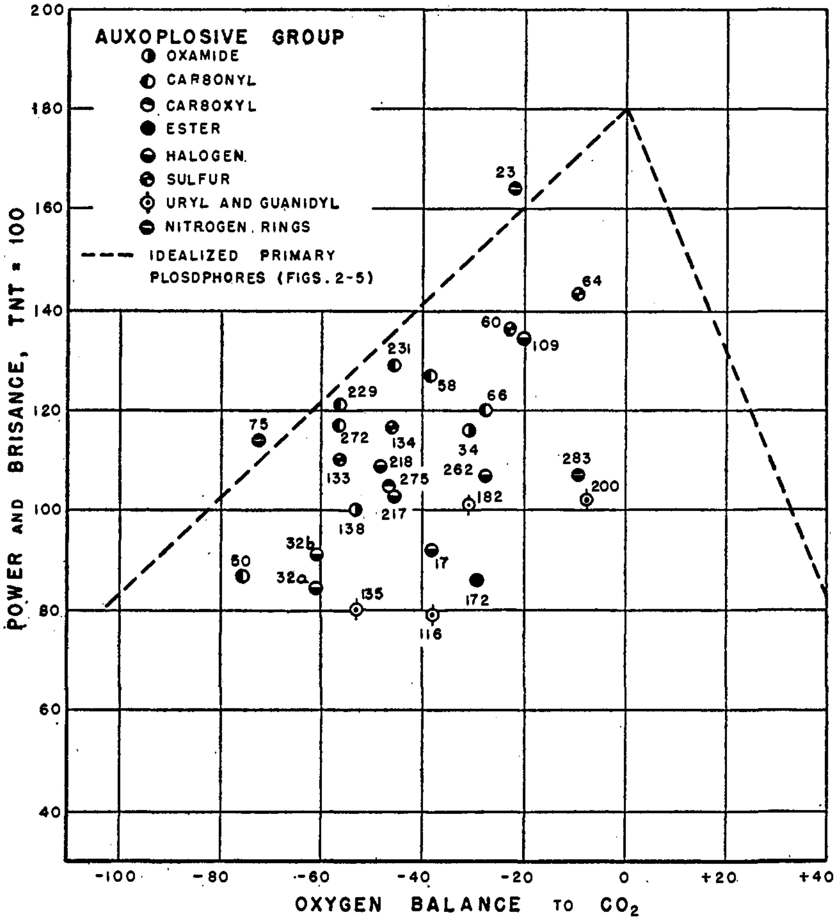


FIG. 9. Effect of auxoplosive groups on power and brisance of primary plosophoric compounds compared with TNT in the lead block expansion test.

Lastly, by either power scheme it can be shown that the effect of positional isomerism causes variations in power which are real but small (i.e., probably less than 10 per cent), while mere molecular size, as would be expected, is of no consequence.

III. CONSTITUTION AND BRISANCE

Employing the concepts of plosophoric and auxoplosive groups one can treat the separate problem of brisance in an analogous manner, although the paucity of data is a serious handicap. This is due chiefly to the lack of a truly satisfactory test which can measure the shattering effect uncomplicated by power. An early method which has lost some favor in recent years is the sand crush test (23). In this procedure a fixed weight of standard sand of known mesh size is enclosed in a bomb and subjected to the shattering action of a standard charge of explosive. The sand crushed is measured by resieving, and the quantities are compared to TNT, as in the case of a self-consistent set of data received by the authors from Picatinny Arsenal. When these data are plotted using the procedures so successful with power, a graph (figure 12) results in which sand crush values for primary plosophores ascend steadily with increasing oxygen balance and display an apparent maximum at the zero point. Secondary and auxoplosive compounds are seen to be inferior.

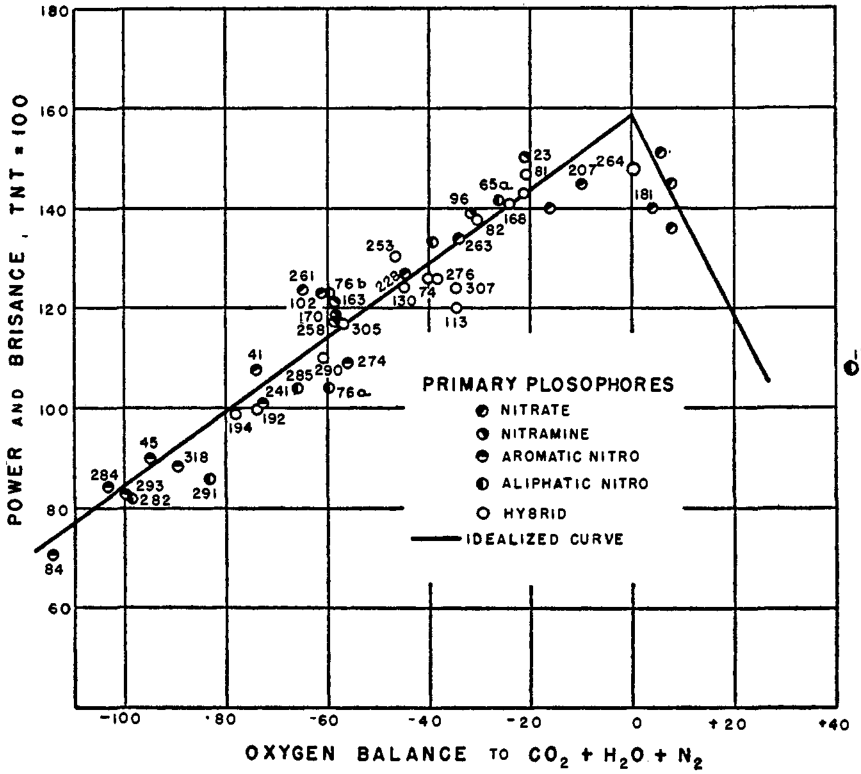


FIG. 10. Effect of oxygen balance on power and brisance of explosives compared with TNT in the ballistic mortar test. Primary and hybrid plosophores.

Less ambiguous but more difficult of quantitative analysis are tests measuring the degree of compression caused in standard lead and copper cylinders by the detonation of a standard charge of explosives placed on top, or tests measuring the depth of penetration of a stack of standard lead sheets when similarly attacked (5).

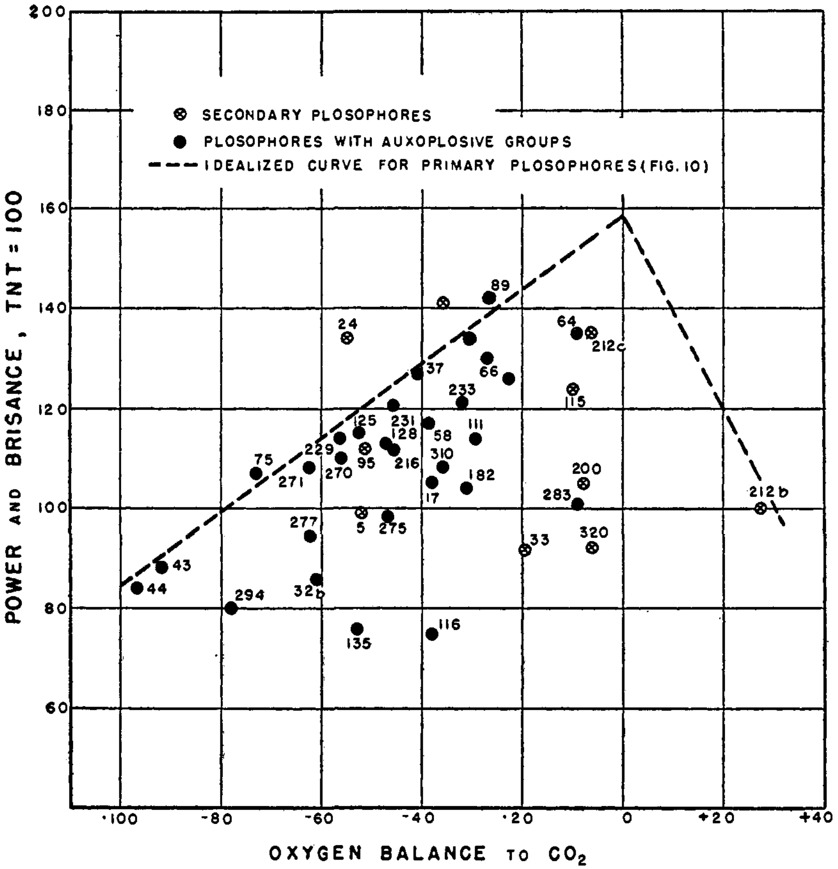


FIG. 11. Effect of oxygen balance on power and brisance of explosives compared with TNT in the ballistic mortar test. Secondary plosophoric and auxoplosive groups.

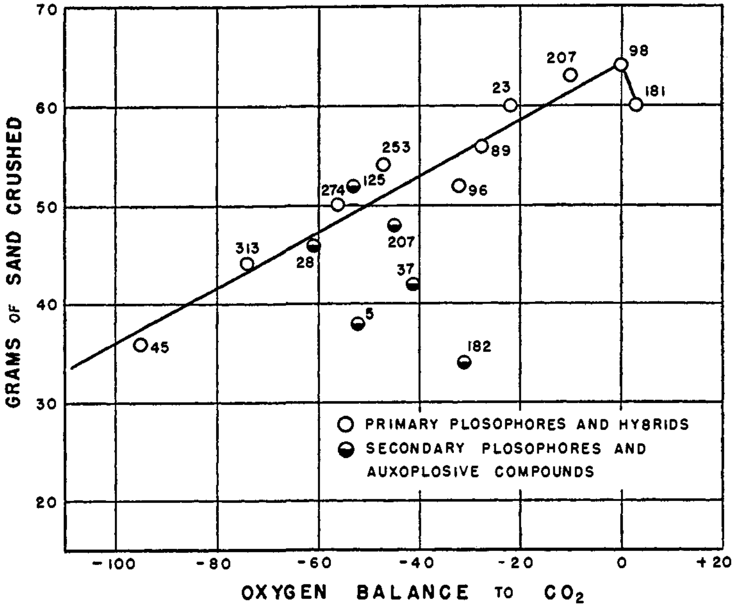


FIG. 12. Measurement of brisance: sand crush *vs.* oxygen balance

Interpretation of such tests is quite subjective, since the appearance of the damage caused is considered significant as well as the depth of penetration. An attempt to circumvent this feature has been made in which a steel plate supported annularly is substituted for lead. The result is a dent rather than a rupture, with the depth of dent being the measure of brisance. Graphical expression of the few data at hand has given results identical with sand crush, thus implying that brisance and power vary simultaneously and in the same direction. It is interesting to note in passing that all plate dent values when plotted against the corresponding ballistic mortar values give a straight line regardless of the presence of plosophoric or auxoplosive substituents. These observations confirm the judgment that power and brisance are twin qualities and that no false conclusions will result from the use of any single test so long as the data are self-consistent.

IV. CONSTITUTION AND OTHER EXPLOSIVE PROPERTIES

A treatment using the same concepts when applied to the properties of detonation velocity and sensitivity yields similar conclusions with somewhat less assurance. In figure 13 observed velocities for all types of explosives are plotted against oxygen balance at a constant loading density of 1.50. In cases where the velocity was measured at a density other than 1.50, a corrected value was obtained by use of the empirical formula $Dd_2 = Dd_1 + 3770(d_2 - d_1)$. There appears to be a drift toward higher velocities as the oxygen balance improves, but the exceptions are numerous. An idealized line has been drawn as a convenience.

It can also be demonstrated that the sensitivity of primary plosophoric and hybrid compounds increases rapidly with increasing oxygen balance, to reach a maximum at the zero balance point. There appears to be a less rapid falling off, however, in the region of positive balance than in the case of power.

The very interesting and valuable piece of work by Roth (20) fully supports all the relationships developed here and in the preceding discussion. Using homogeneous mixtures of tetranitromethane (a liquid of very high oxygen balance) and nitrobenzene (a liquid of very low oxygen balance), the whole range of oxygen balance was investigated and it was shown that power (lead block), detonation velocity, brisance (lead plate), and sensitivity all reach their maximum values at or very close to the point of zero oxygen balance. Of these qualities only sensitivity failed to diminish in the region of positive balance. The implications of these observations for military use are unfortunate, in that the most powerful explosives will also be expected to be the most sensitive.

On the same sensitivity scale, auxoplosive compounds are found to be slightly more variable than pure plosophoric types but otherwise similar. It is among the secondary plosophores that one encounters unpredictable behavior. Here the effect of different chemical groupings is a real one and is superimposed on that of oxygen balance, so that sensitivity is tied up to a variable and large degree with the specific identity of the substituent secondary plosophore. Azides are notably sensitive examples and hence find usefulness as initiators.

Although it would be particularly desirable to relate chemical stability to other parameters, it has not proved possible to do so except in a very rough manner, as has been done in the past. *A priori* it can be said that nitrate esters are generally unstable, that primary nitramines are less stable than secondary, that aliphatic nitro compounds are most stable when they lack enolizable hydrogen, etc. These observations have been made before and no available quantitative data appear sufficient to improve upon them or to reduce them to more definite terms.

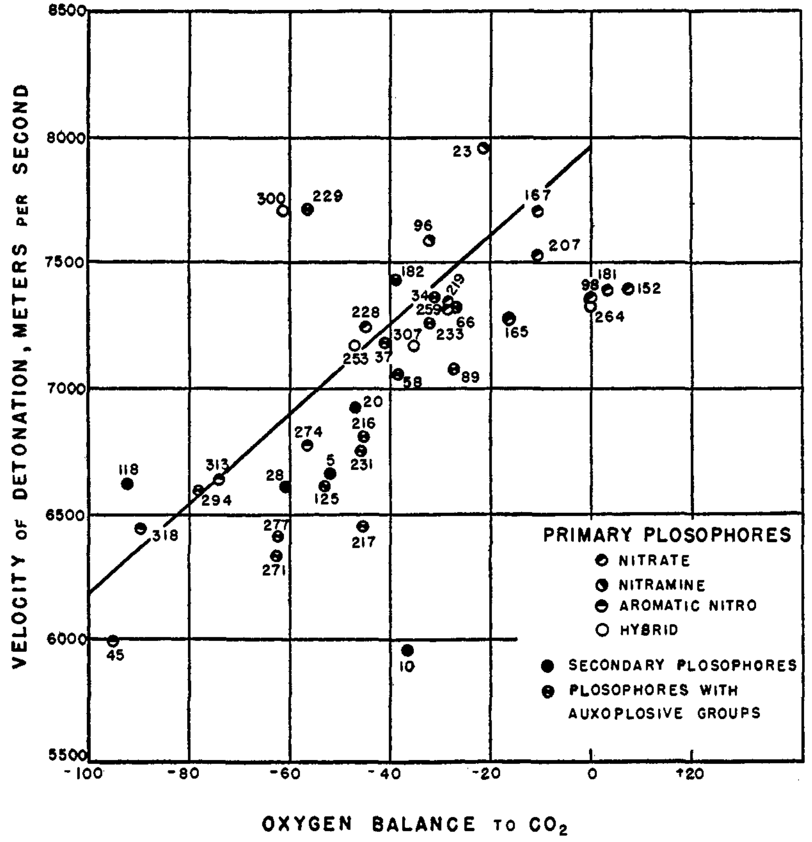
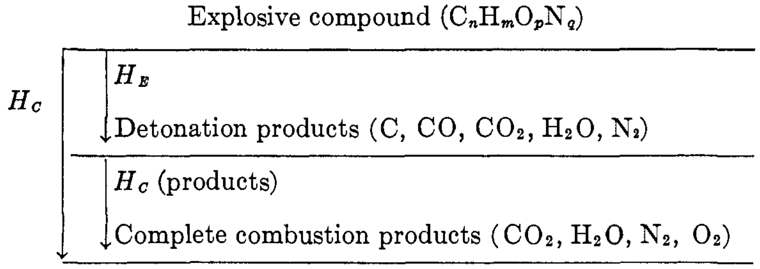


FIG. 13. Effect of oxygen balance on detonation velocity at a loading density of 1.50

V. CONSTITUTION AND HEAT OF EXPLOSION

The foregoing treatment of the subject, using plosophores and oxygen balance, has amounted to a rough system of thermodynamics. It is appropriate, therefore, to analyze the problem from that viewpoint and to reduce the qualitative theory to a quantitative basis. Such an approach is not original, having been developed essentially in its main outline during the last century (1). In the interest of completeness, however, it is briefly recapitulated here to permit a direct comparison with the organic approach given above. Of various energy terms which may be considered, the one known as the *heat of explosion* (H_E) must be the most significant, for by definition it is the energy liberated when the explosive compound is detonated to produce its detonation products. In practice this energy is difficult to measure directly, although it has been successfully accomplished by the use of a bomb calorimeter of adequate strength (19). Fortunately, it may be very closely approximated by a simple calculation from the heat of combustion (H_C) as determined by standard calorimetry methods (7, 18, 17, 24). In the following diagram the energy levels and the changes in energy in passing from one level to another are shown. The various H terms correspond to $-\Delta E$ in standard usage.



From this it is clear that $H_E = H_C - H_{C(\text{products})}$ and that the last term should be easily obtained, since the values for the oxidation of the partially oxidized detonation products (hydrogen, carbon, carbon monoxide) are known with great accuracy.

This method of obtaining H_E requires that one know what the products of detonation are and the extent to which they are formed, and this in turn necessitates either an extremely difficult experimental technique which has yet to be devised or a reasonable assumption designed to allow a simple treatment of the problem. Fortunately the latter method in practice appears to be sufficient for all practical purposes.

In the light of the water gas reaction it can be assumed that, when an explosive detonates, the oxygen present combines first with the carbon to form carbon monoxide, then with the hydrogen to form water, and finally with the carbon monoxide to form carbon dioxide (9, 21, 25). The water formed is considered to be gaseous, as it is under the explosion conditions. In compounds of negative balance these reactions can be considered as occurring in steps and only so far as the oxygen will allow. In compounds of zero balance, the detonation products will coincide with the final combustion products, for then $H_{C(\text{products})}$ will equal zero and H_E will equal H_C.

There are grounds to doubt that the above assumption is correct to better than 15 per cent, and some investigators (2) have preferred an arrangement of reactions in which at least part of the hydrogen present is first converted to water, followed by oxidation of the carbon to carbon monoxide and then to carbon dioxide. Others have applied an arbitrary correction factor. The actual performance of specific explosives presumably lies at some indeterminate position between the extreme assumptions. In any case the differences due to the various assumptions will diminish with increasing oxygen balance and will disappear entirely at the point where oxygen is sufficient to convert all the hydrogen to water and all the carbon to carbon monoxide. This is the so-called carbon monoxide point and corresponds in oxygen balance to about −20 to −25 per cent. In the range of oxygen balance of greatest apparent interest, therefore, the difficulty does not exist.

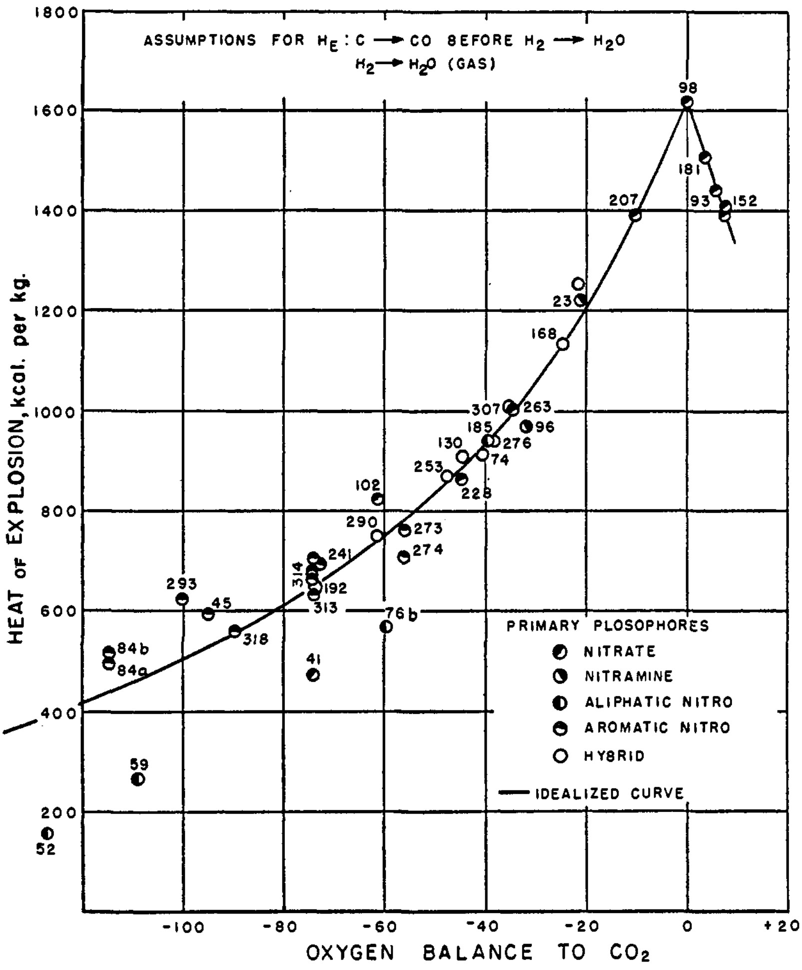


FIG. 14. Heat of explosion *vs.* oxygen balance for primary plosophores and their hybrids

Using the first assumption with all explosives for which heat of combustion values have been available, H_E has been calculated on a weight basis and the resulting H_E values for primary plosophoric and hybrid molecules have been plotted against oxygen balance, yielding figure 14. It is seen that the heat of explosion varies directly with oxygen balance for these compounds, reaches a maximum value at zero balance (10), and in general resembles the power curves of figure 1. The results of a similar treatment of secondary plosophoric and auxoplosive compounds are given in figure 15. The poor showing of most of these in comparison with the idealized primary plosophoric curve is attributable to the partial combustion states that such groups represent and is the explanation for their generally unfavorable nature.

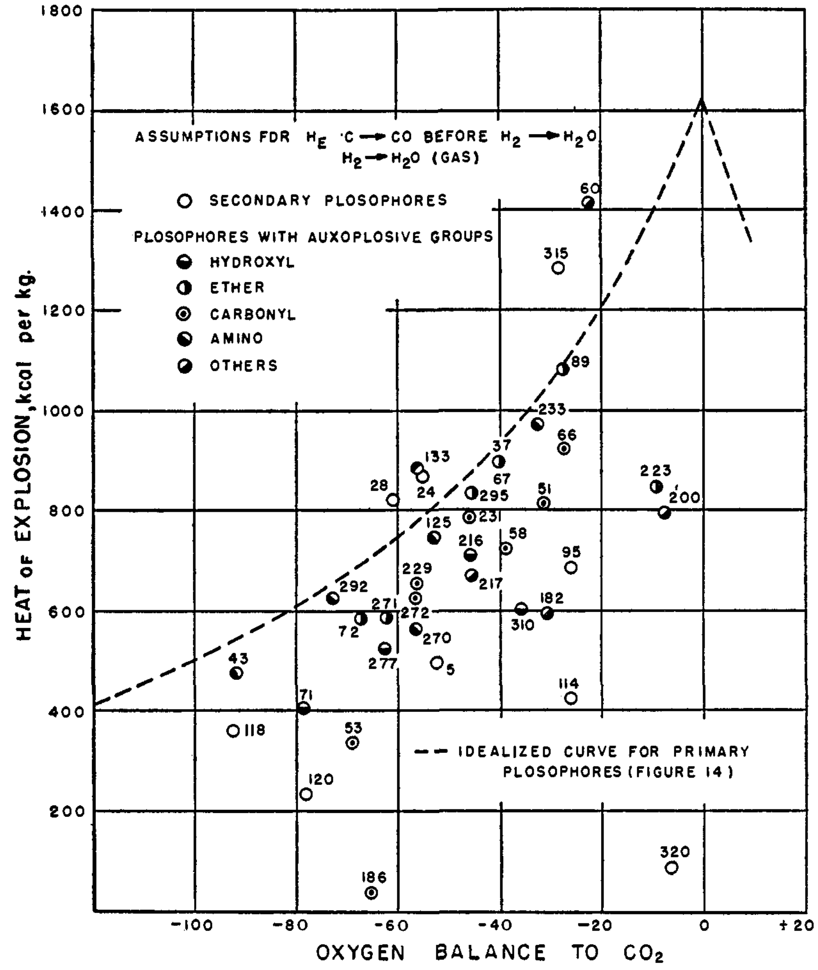


Fig. 15. Heat of explosion *vs.* oxygen balance for secondary plosophores and primary plosophores with auxoplosive groups.

The conclusions reached above from organic chemical considerations are explained and, as has been well known in the past, H_E is seen to be directly related to power (4). This last point is illustrated by figures 16 and 17, which present the relationship between lead block or ballistic mortar performance and heat of explosion together with idealized curves obtained by inspection.

With this point established, we have completed our objective of connecting the performance of explosives with their constitutions and with few exceptions have found the existing data consistent with the treatment developed. It remains, however, to extend the scope of the system to the prediction of power in advance of synthesis. By methods which are not novel (8, 21) but the details of which will not be presented here, it is possible to derive H_C values for each structural feature commonly present in primary plosophoric and hybrid explosives. In accord with standard thermodynamic reasoning, summation of the appropriate individual values for all the features of specified structure then yields the H_C value of the proposed explosive with an accuracy estimated to be ± 1 per cent and a maximum deviation of less than ± 3 per cent. From such a

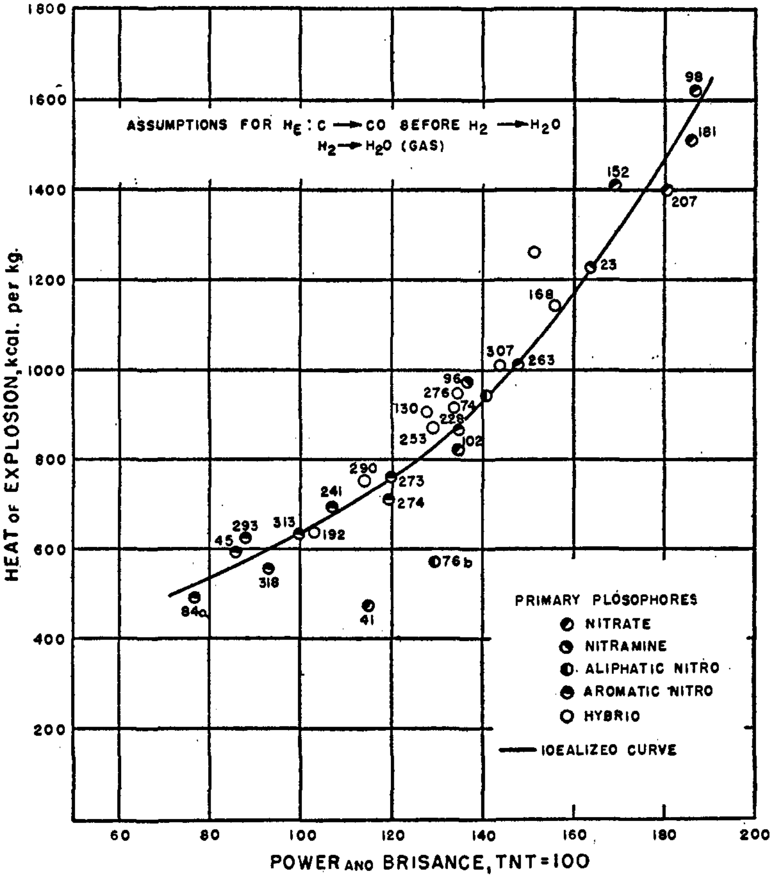


FIG. 16. Heat of explosion *vs.* power and brisance (lead block expansion test) of primary plosophores and their hybrids.

calculated value H_E may be obtained by the usual methods, and through figures 16 and 17 the expected power performance can then be estimated. Thus one has prior to synthesis a method of predicting performance of compounds containing the molecular structures reported.

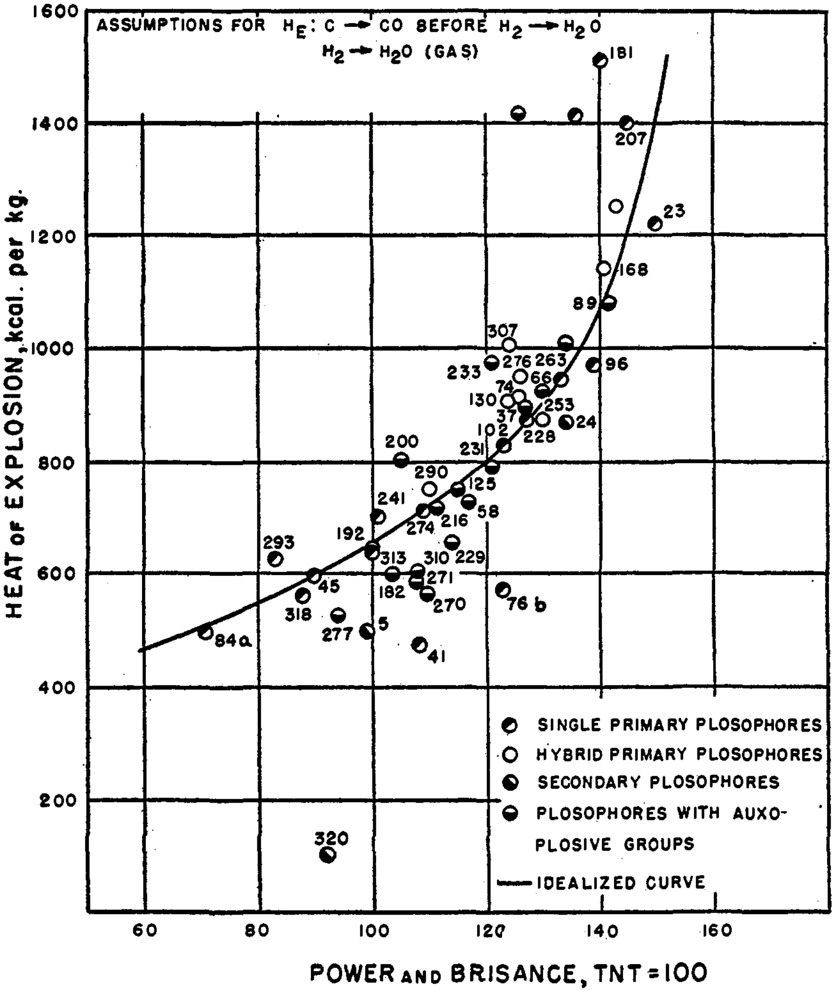


FIG. 17. Heat of explosion *vs.* power and brisance (ballistic mortar) of plosophoric compounds.

One might assume also that figures 1 to 5 or figure 10 would supply the power of a proposed structure directly from oxygen balance provided only primary plosophores are present. While use of these idealized curves will yield a reasonable prediction of performance for primary plosophoric and hybrid molecules, it is certain that the value which can be calculated will be a better approximation. One should probably not infer that either method is of such accuracy that further research looking toward the discovery of more powerful organic explosives is unwarranted, especially since the region of greatest interest (between −20 per cent and ± 0 per cent in oxygen balance) has been so little explored. Furthermore, the remarks made here are based entirely on presently available data, which, while intended to be complete, do not disclose fully the considerable advances in explosives theory made during the war nor contain examples of all appropriate groups which might be introduced into explosive molecules. There are also a number of assumptions which have entered into the thermodynamic treatment of the problem and whose net effect has not been accurately estimated. It is quite conceivable that future work will show that certain new arrangements of atoms may give enhanced performance beyond that which would be expected from oxygen balance or from *calculated* heat of combustion.

VI. SUMMARY

Much available data on the power of pure organic explosives have been assembled and interpreted. Using the terms oxygen balance, plosophoric and auxoplosive groups, and heat of explosion, the types of molecules have been defined which appear of synthetic interest for use as high explosives. It is hoped that the new qualitative treatment of the subject will prove a stimulation to renewed synthetic organic research in a difficult field.

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