hindered skeletal internal rotations for these activated complexes.

Finally the excellent agreement between theory and experiment for reaction 9 between Br and H_2 and the 100,000 fold discrepancy between calculated and observed factors for reaction 10

$$(CH_3)_3CH + Br \longrightarrow (CH_3)_3C + HBr$$

require special comment. We make an unqualified prediction that the observed value is wrong; in particular, we believe a reinvestigation of this reaction over a wide range of reactant pressure, degree of reaction, and pressure of additives will reveal that the over-all reaction $(CH_3)_3CH + Br_2 \rightarrow (CH_3)_3CBr + HBr$ does not follow the bromination mechanism assumed for it.[10]

Evaluation.—Kinetic data are often so uncertain that order-of-magnitude estimates of pre-exponential factors are all that one can obtain from experiment. There are many empirical rules and approximation methods in the field of molecular structure and molecular spectroscopy which, though not good enough for many purposes in their own field, are more than adequate for purposes of kinetics. The rules used here for bond distances,[5,6] for stretching force constants,[6a] and for moments of inertia for internal rotation[4] appear to be cases of this type. However, we kineticists must await developments for comparable rules for barriers to internal rotation and for either a Badger's rule for bending force constants or, more likely, an adequate empirical classification of bending frequencies. With such rules, kinetic pre-exponential factors should be calculable within a factor of four or so, without undue labor, even for complicated reactant molecules. At present these calculations appear to be valid within, perhaps, a factor of about 40. It might be remarked that for practical purposes this situation is a considerable improvement over the case as stated recently by Trotman-Dickenson[11] relative to reaction 10.

(11) A. F. Trotman-Dickenson, "Gas Kinetics," Academic Press, Inc., New York, N. Y., 1955, p. 194, line 13.

STANFORD, CAL.

[CONTRIBUTION FROM THE EXPLOSIVES RESEARCH GROUP, UNIVERSITY OF UTAH]

Velocity–Diameter Curves, Velocity Transients and Reaction Rates in PETN, RDX, EDNA and Tetryl[1]

BY MELVIN A. COOK, ROBERT T. KEYES, WILLIAM S. PARTRIDGE AND W. O. URSENBACH

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Velocity-diameter $D(d)$ curves for cap initiated, low density PETN (Pentaerythratol Tetranitrate), RDX (Cyclotrimethylene trinitramine), EDNA (Ethylene dinitramine) and Tetryl (Trinitrophenylmethylnitramine) are presented. Analysis of these curves by the theories extant of chemical reaction rates in detonation gave total reaction times ($\tau = Mc\bar{R}_g$) expressed by average M values of 8.0×10^{-5}, 7.5×10^{-5}, 1.5×10^{-4}, and 2.5×10^{-4} sec./cm. for PETN, RDX, tetryl and EDNA, respectively; and c values of 1.0, ~0.1, and ~0.04 for the geometrical model, nozzle theory and curved front theory, respectively. ($\bar{R}_g$ is the average grain radius.) Low-order detonation was observed in both tetryl and EDNA in the "non-ideal" detonation region and slightly into the "ideal" region for charge lengths less than 2 to 5 cm. and diameters less than 3 to 5 cm. At the end of this low-order regime detonation changed over abruptly to normal high-order detonation in all except the smallest diameter charges of coarse tetryl where the high and low-order detonation curves could not be resolved.

Aside from their practical value, velocity–diameter or $D(d)$ curves have theoretical value in providing (by curve fitting) the parameter τ (total reaction time), or a_0 (reaction zone length), occurring in the various theoretical models of reaction rates in detonation, namely, the "nozzle" theory,[2] the "curved front"[3] theory and the "geometrical" model.[4] Moreover, comparisons of the theoretical and observed $D(d)$ curves are helpful in evaluating these theories. Previous such applications have been carried out in this Laboratory for TNT,[4a] DNT,[5] AN in the pure state and in TNT and Composition B,[6] sodium nitrate in TNT,[7] and for barium nitrate, lead nitrate, aluminum and other ingredients in TNT and in some cases, Composition B.

This paper presents velocity–diameter curves for low density PETN, RDX, tetryl, and EDNA together with the reaction rates computed by means of the three published models of reaction rates in detonation. Presented also are experimental data concerning a velocity transient observed to occur in the early stages of the detonation process in the small diameter charges of low density, cap initiated tetryl and EDNA. Another factor of importance in evaluating and applying the curved front theory aside from the $D(d)$ curves is the steady-state shape of the detonation wave. Experimental wave shape results with these and other explosives were presented by Cook, *et al.*[8]

Experimental Methods and Results

The explosives used in this study were of the highest (service) available purity and were screened using U. S. standard Tyler screens. The screen cuts used for PETN were −35 +48 mesh and −65 +100 mesh, −65 +100 mesh

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(1) This investigation was supported by Office of Naval Research, Contract No. N7-onr-45107, Project No. 357239.

(2) H. Jones, *Proc. Roy. Soc.* (*London*), **189A**, 415 (1947).

(3) H. Eyring, R. E. Powell, G. H. Duffey and R. B. Parlin, *Chem. Revs.*, **45**, 69 (1949).

(4) (a) M. A. Cook, G. S. Horsley, W. S. Partridge and W. O. Ursenbach, *J. Chem. Phys.*, **24**, 60 (1956); (b) M. A. Cook and F. A. Olson, *J. Am. Inst. Chem. Eng.*, **1**, 391 (1955).

(5) M. A. Cook and W. S. Partridge, *J. Phys. Chem.*, **59**, 673 (1955).

(6) M. A. Cook, E. B. Mayfield and W. S. Partridge, *ibid.*, **59**, 675 (1955).

(7) M. A. Cook and W. O. Ursenbach, Paper No. 25, Second ONR symposium on Detonation, Feb. 9–11, 1955, Washington, D. C.

(8) M. A. Cook, G. S. Horsley, R. T. Keyes, W. S. Partridge and W. O. Ursenbach, *J. Appl. Phys.*, **27**, 269 (1956).

TABLE Ia

MEASURED $D(d)$ DATA FOR PETN, RDX AND EDNA

	PETN				RDX		EDNA				
					−65 + 100 mesh		−35 + 40 mesh			−65 + 100 mesh	
d, cm.	ρ_1 (g./cm.^{3})	D (mm./μsec.)	ρ_1 (g./cm.^{3})	D (mm./μsec.)	ρ_1 (g./cm.^{3})	D (mm./μsec.)	ρ_1 (g./cm.^{3})	D_t (mm./μsec.)	D (mm./μsec.)	ρ_1 (g./cm.^{3})	D (mm./μsec.)
0.318	0.914	4.24	1.00	4.94	1.25	5.69				1.0	F[a]
	.914	4.18	1.0	5.10	1.26	5.50					
.635	.964	5.16	1.016	5.41	1.21	6.37	1.025	2.81	[b]	0.996	4.15
	.970	5.09	0.954	5.20	1.21	6.40	0.997	2.60		1.017	3.52
							1.01	[c]	3.44		
							1.00	[c]	3.49		
.953	.960	5.29	1.017	5.51	1.17	6.68	1.002	..	4.08	0.988	5.03
	.960	5.31	1.002	5.41	1.16	6.60	1.008	..	4.83	.990	5.25
							1.020	3.24	4.80		
							1.000	3.41	4.98		
1.27	.950	5.31	0.991	5.40	1.22	6.72	0.985	[c]	5.26	.994	5.36
	.971	5.31	.960	5.41	1.22	6.72	.931	[c]	5.00	.991	5.50
							1.00	4.15	5.20		
							1.00	3.74	5.24		
1.59	.961	5.41	.974	5.38	1.19	6.70	0.954	[c]	5.16	.971	5.48
	.921	5.31	.964	5.46	1.17	6.51	.977	[c]	5.30	.981	5.52
							1.03	4.40	5.36		
							1.03	4.25	5.24		
1.90	.920	5.13	.996	5.51	1.15	6.58	0.980	[c]	5.46	.959	5.31
	.943	5.26	.989	5.44	1.15	6.56	.970	[c]	5.43	.967	5.49
							1.00	4.61	5.56		
							1.00	4.45	5.58		
2.22	.909	5.23	.979	5.48	1.16	6.49	0.960	[c]	5.28	.966	5.44
	.915	5.32			1.16	6.53	.979	[c]	5.47	.965	5.51
							1.00	4.82	5.56		
							1.01		5.60		
2.54	.926	5.26			..	6.47	0.976	[c]	5.58	.98	5.59
	.941	5.30			1.14	6.42	.976	[c]	5.53	.97	5.63
							1.00		5.61		
							1.01	4.98	5.64		
7.54										1.064	6.12
										1.059	6.10
19.89										1.059	5.90
										1.048	5.97
										1.045	5.90
										1.054	5.92
										0.98	5.76
										.99	5.78

[a] F = failed; D_t = transient or low-order velocity. [b] Two detonation failures occurred in this diameter, but the low-order transient (or the normal wave) persisted the length of the charge in these two shots. [c] These shots measured at $L/d > 3$ before transient was observed.

for RDX, −20 +28 mesh and −35 +48 mesh for tetryl, and −35 +48 and −65 +100 mesh for EDNA. Charges were loose-packed (vibrated for density uniformity) in plastic tubing of wall thickness $^1/_{32}''$ for $d < 1$ cm., plastic tubing of wall thickness $^1/_{16}''$ for $1 \leqslant d \leqslant 2.5$ cm., and manila paper tubes for $d > 2.5$ cm. Tubes of $d \leqslant 2.5$ cm. were all 15 ± 0.4 cm. in length and those of $d > 2.5$ cm. were six or more diameters in length. Densities were determined in all cases by weight-volume measurements. Velocities were measured by means of a rotating mirror ("streak") camera of film writing speed up to 5 mm./μsec. except for the shots of $d >$ 7.5 cm. where a "pin-oscillograph" capable of measuring times to 0.01 μsec. was used. The "pin" method was considered unsatisfactory for use in very small diameter charges owing to a possible adverse influence of pin inserts on wave propagation in very small diameter charges.

While velocities were measurable by the methods used here with an accuracy of about ±0.1%, the reproducibility of results was considerably less accurate (about ±1 to 2%) owing to the influence of unavoidable density fluctuations in the loose-packed explosives. Table I summarizes the $D(d)$ data obtained in this investigation.

In order to obtain velocities at the nearest even densities, density corrections by means of the equation

$$D_{\rho_e} = D_{\rho_1} + S(\rho_e - \rho_1) \qquad (1)$$

were made, where D_{ρ_1} is the velocity measured at the density ρ_1 and D_{ρ_e} is that at the nearest round value ρ_e of density.

The average large diameter (ideal) velocity D^* may be expressed by the linear relation

$$D^* = D_{1.0} + S(\rho_1 - 1.0) \qquad (2)$$

with values of the parameters $D_{1.0}$ and S given in Table II.

The $D(d)$ results for PETN and RDX corrected to ρ_1 = 0.95 g./cc. and 1.2 g./cc., respectively, are shown in Fig. 1.

In both tetryl and EDNA at diameters from the critical one (d_c) to slightly above $d_m{}^*$ (minimum diameter for $D = D^*$, where D^* is the "ideal" or "hydrodynamic" velocity) the wave commenced propagating at low velocity (low-order detonation), but suddenly changed over to the normal high velocity or high-order detonation at a point from 2 to 5 cm. from the point of initiation. The traces in each case where this dual velocity effect was observed showed two straight line sections. In early studies, however, velocities

Table Ib

Measured $D(d)$ Data for Tetryl

	−20 + 28 mesh			−35 + 48 mesh		
d, cm.	ρ_1, (g./cm.³)	D_t (mm./µsec.)	D (mm./µsec.)	ρ_1 (g./cm.³)	D_t (mm./µsec.)	D (g./cm.³)
0.318	. . .	. .		0.972		F
0.635	0.96		F	0.98		4.88
0.933	0.952	1.51	1.51	0.958		5.27
	.952	1.97	1.97	1.007		5.14
	.961	1.98	1.98	0.965	2.62	4.90
				1.003	2.55	4.96
1.27	0.965	1.97		0.974	. .	5.40
	.988	1.95		.956	. .	5.36
	.916	. .	4.35	.886	2.57	5.13
	.927	. .	4.33	.910	2.44	5.12
1.59	.907	2.30	4.96	.958		5.44
	.908	2.26	4.77	.956		5.54
	.961	2.46	4.45	.934	. .	5.04
				.732	. .	5.19
1.905	.955	2.65	5.28	.978	. .	5.43
	.926	2.42	. .	.958	3.51	5.15
	.916	2.33	5.11	.955	3.37	5.24
	.934	2.34	4.86			
2.222	.939	2.41	5.16	.972	. .	4.98
	.925	2.66	5.12	.940	. .	5.11
	.926	2.60	4.98	.948	4.41	5.31
	.924	2.13	5.03	.948	4.70	5.23
2.54	.952	2.51	5.21	.967	. .	5.41
	.960	1.93	5.20	.956	4.54	5.18
	.932	2.38	5.00	.966	3.91	5.25
	.918	2.38	5.10			
	.990	2.44	5.11			
3.18	.918	. .	4.94	.964	. .	5.39
				.931	. .	5.28
3.80				.932	. .	5.34
				.930	4.64	5.36
4.39	.96	2.95	5.21	1.013	. .	5.55
	.963	3.09	4.93	1.013	. .	5.60
5.04	.891	3.67	5.04	1.034	. .	5.56
	.846	3.65	4.70	1.031	. .	5.40
6.30	.815	. .	4.98	1.020	. .	5.45
	.815	. .	4.83	1.012	. .	5.54
7.54	.820	. .	4.88	1.001	. .	5.58
	1.00	. .	5.54	0.970	. .	5.46

Table II

Parameters of $D(\rho_1)$ Curve (Equation 2)[a]

	$D_{1.0}$ (m./sec.) (1)	$D_{1.0}$ (m./sec.) (2)	S (m./sec./g./cc.) (1)	S (m./sec./g./cc.) (2)
PETN	5550	5550	3950	3950
Tetryl	5550	5600	3350	3350
RDX	6000	6080	3580	3590
EDNA	5765	5910	3635	3275

[a] (1) This investigation; (2) NDRC Report OSRD 5611.

were measured only beyond about three diameters, and this velocity transient was thus not observed in these cases. The low-order detonation, as in normal high-order detonation, was constant in velocity. Similar velocity transients were observed by Jones and Mitchell[9] using small boosters. They showed that the distance of the low-order regime fell off progressively as the size of the booster increased until finally with a large enough booster it disappeared altogether. In this study only cap initiation without boosters was used. The distance from the point of initiation to the point of sudden transition was measured in each case where dual velocities were observed and the results are summarized in Table III. The low-order regime may perhaps be attributed to a metastable equilibrium or to non-equilibrium in the gaseous products in the early stages of detonation before the detonation wave reaches maximum intensity.

The velocity-diameter data both in the low-order regime and in the steady-state region (beyond the transition from low-order to normal detonation) are plotted for tetryl (corrected to $\rho_1 = 0.95$) in Fig. 2 and for EDNA (corrected to $\rho_1 = 1.0$) in Fig. 3.

Table III

Distance S' from Point of Initiation to Point of Disappearance of Low-order Regime (in Centimeters)

	S' for Tetryl		S' for EDNA	
Diameter (cm.)	−20 + 28 mesh	−35 + 48 mesh	− 35 + 48 mesh	−65 + 100 mesh
0.95	[a]	4.6	2.5	No transient
1.27	[a]	3.0	2.3	No transient
1.59	4.5	3.4	2.3	No transient
1.90	4.4	2.1	2.1	No transient
2.22	4.4	1.7	2.2	No transient
2.54	4.5	2.2	2.0	No transient
4.39	4.3	2.2	No definite transient	No transient
5.04	4.0	No transient		No transient

[a] The normal velocity was low in these cases owing to the influence of incomplete reaction and the low velocity and normal velocity regimes could not, therefore, be resolved.

Interpretation of Results

The equations of the curved front, nozzle and geometrical models of reaction rates in detonation are presented elsewhere.[4a,5] All three involve an empirical parameter τ or a_0 given, according to experimental evidence by the equation

$$\tau = Mc\bar{R}_g = \bar{R}_g/\lambda k' \tag{3}$$

or

$$a_0 = M'c\bar{R}_g = 3D\bar{R}_g/4\lambda k'$$

of the Eyring surface erosion model. Here k' is given by the equation

$$k' = \frac{kT}{h} e^{\Delta S^*/R} e^{-\Delta H^*/RT} \tag{4}$$

and λ is the average diameter of the explosive molecule. The geometrical model also takes into account an edge effect of 0.6 cm. in unconfined charges. A similar correction although not yet applied is clearly needed in the nozzle and curved front theories.[4a] In confined charges this edge effect[4b] is less than 0.6 cm. and becomes zero with sufficiently large confinement. Equation 3 has been shown previously to apply within experimental error as regards $\tau(\bar{R}_g)$ for a given explosive.[4a,5–7] The values of the total reaction time τ, obtained by applying the nozzle, curved front and geometrical models to the experimental data of this study, expressed in terms of the average particle radius $\bar{R}_g$ are given within experimental error by equations 3 using $(\lambda k')^{-1}$ values as follows: $8.0 \times 10^{-5}\, c$ (PETN); $7.5 \times 10^{-5}\, c$ (RDX); $1.5 \times 10^{-4}\, c$ (tetryl); $2.5 \times 10^{-4}\, c$ (EDNA), where $c = 1.0$ for the geometrical model, about 0.1 for the nozzle theory and about 0.04 for the curved front theory. The actual calculated data are summarized in Table IV from which one may estimate the reliability of these values of c and the validity of equation 3.

Comparison of k' (Detonation) with k' (Thermal Decomposition).—It is of interest to compare the specific rate constants $k'(T)$, extrapolated by

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[9] H. Jones and Mitchell, *Nature*, **161**, 98 (1958).

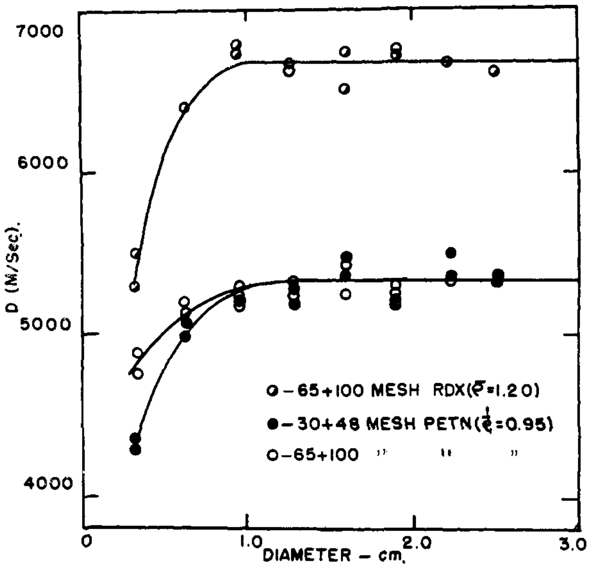

Fig. 1.—*D–d* curves for RDX and PETN.

means of the Eyring absolute reaction rate theory to the detonation temperature, with k' values obtained from the nozzle, curved front and geometrical models of reaction rates in detonation. Before carrying out this extrapolation, however, let us consider briefly the nature of thermal decomposition data. Isothermal decomposition studies carried out in this Laboratory[10] have shown that in those explosives that obeyed accurately the first-order decomposition law, for example, TNT, AN and hydrazine mononitrate, over most or all of their isothermal decomposition curves the value $kTe^{-\Delta S^*/h}$ was about $10^{9.6}$ (sec. °K.)$^{-1}$. From equation 4 this corresponds to an entropy of activation of about -3.2 e.u. for these explosives. On the other hand PETN, RDX and tetryl exhibited in isothermal decomposition strong autocatalytic effects. In the case of EDNA combinations of autocatalytic and auto-inhibitory effects were observed although in this case it was possible to observe the uncatalyzed, first-order decomposition in the early stages of decomposition. A' was found in EDNA to be $10^{8.5}$ corresponding to $\Delta S^* = -8.3$ e.u. But when attempts were made to determine $k'(T)$ from the autocatalyzed portion of the decomposition curve by application of the first-order law, much larger valus of A' as well as ΔH^* were obtained. Thus, for EDNA values of A' and ΔH^* obtained from the strongly autocatalyzed part of the curve were 10^{29} (sec. °K.)$^{-1}$ and 71.7 kcal./mole, respectively, compared with respective values of $10^{8.5}$ and 30.8 for the true first-order part of the decomposition curve observed during the first approximately 5% of the decomposition. (Note, however, that despite these great differences the k's were actually not much different.) In the past the decomposition of explosives of this type as well as primary explosives has usually been treated as first order. There exists considerable evidence moreover, that the first-order law should be quite generally applicable in the thermal decomposition of explosives under conditions where autocatalysis and similar effects do not enter to upset the first-order law. Autocatalysis results, however, in excessive values of A' and ΔH^* (and such as to keep k' almost the same). Thus for tetryl Robertson[11] obtained $A' = 10^{12.70}$ (sec. °K.)$^{-1}$ and $\Delta H^* = 38.4$ kcal./mole while Rojinsky[12] using conditions less likely to apply to the true first-order decomposition found $A' = 10^{24.8}$ and ΔH^* 60 kcal./mole. On the other hand, by operating at the lowest possible temperatures and evaluating the constants from data determined only in the earliest stages of decomposition where autocatalysis was least important, Cook and Abegg found $A' = 10^{10.3}$ and $\Delta H^* = 34.9$. Even under these conditions the decomposition was still complicated by some auto-

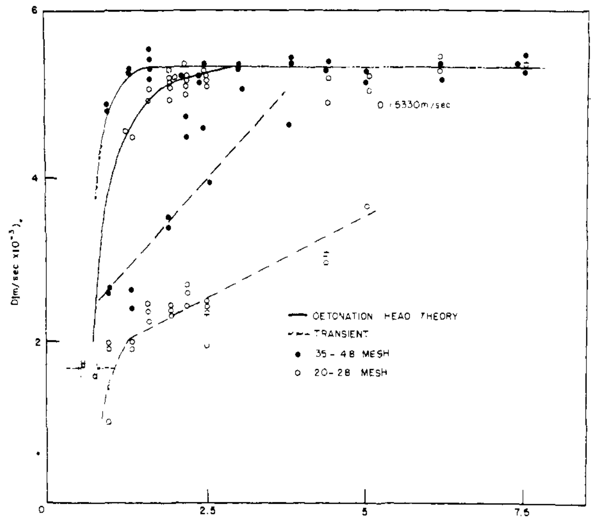

Fig. 2.—*D*(*d*) curve for tetryl.

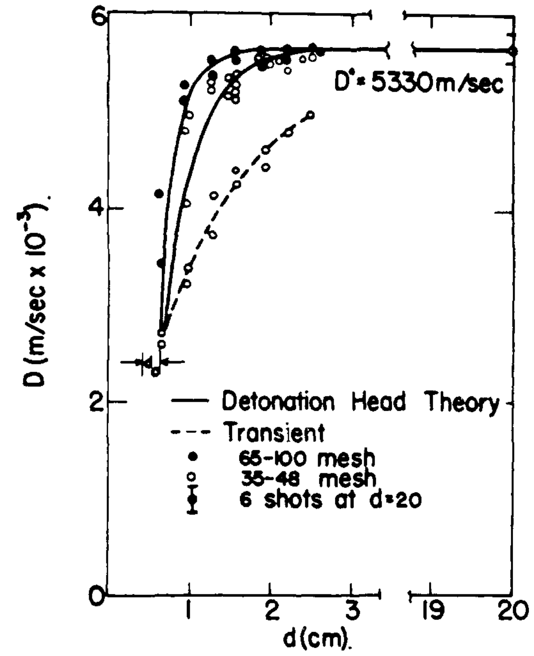

Fig. 3.—*D–d* curves for EDNA.

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(10) M. A. Cook and M. T. Abegg, *Ind. Eng. Chem.*, **48**, 1090 (1956).

(11) E. K. Rideal and A. J. B. Robertson, *Proc. Roy. Soc.* (*London*), **A195**, 135 (1948).

(12) S. Rojinsky, *Z. physik. Chem.*, **B18**, 364 (1932).

TABLE IV

REACTION RATES OF PETN, RDX, TETRYL AND EDNA IN DETONATION

Explosive	Size (Standard Tyler mesh)	Nozzle theory a_0 (mm.)	Nozzle theory τ (μsec.)	Curved front theory a_0 (mm.)	Curved front theory τ (μsec.)	Geometrical model τ (μsec.)	Geometrical model q^b (mm.)
PETN	-35 ± 48	1.0 ± 0.2^a	0.21	0.5 ± 0.1^a	0.093	2.1	2
	-65 ± 100	$0.9 \pm .2$	.17	$.4 \pm .1$	.075	1.5	2
RDX	-65 ± 100	$1.0 \pm .2$	.15	$.4 \pm .2$	.06	1.4	2
EDNA	-35 ± 48	$3.5 \pm .3$	.06	$2.0 \pm .6$	.35	6.0	5
	-65 ± 100	$3.0 \pm .5$	.52	$1.5 \pm .5$	.26	3.5	5
Tetryl	-20 ± 28	4.0 ± 1.5	.70	....	...	4.1	6
	-35 ± 40	2.5 ± 1.0	.40	....	...	2.5	6

[a] Values show spread from computed a_0 across curve. (a_0 = reaction zone length). [b] q = "edge effect," *i.e.*, $q = d - d'$ where d' is effective diameter. This has been found generally to be 6 mm. in unconfined charges and less in confined ones. The relative confinement in this study was large in the smallest diameters accounting for the low edge effect for RDX and PETN.

catalysis. Note, however, that despite the great differences in A' and ΔH^* in these three investigations the k' values at the temperatures at which the measurements were actually carried out were all in agreement within an order of magnitude. Comparable results were found for RDX and PETN[10,13] and one generally finds that the lower the temperature and the smaller the amount of decomposition over which one studies the decomposition rate, the lower are the values one obtains for both A' and ΔH^*, if the results are interpreted by the first-order law. Actually, the proof that PETN, RDX and Tetryl do not actually decompose isothermally following a first-order law in isothermal measurements at T 130–180°, where strong autocatalysis was observed, is shown by Figures 4, 5, and 7, Ref. 10, and the published data pertaining to $k'(T)$ where autocatalysis is involved are, therefore, not generally valid for these explosives. However, under conditions in which autocatalysis was minimized A' and ΔH^* were found to be much lower than when stronger autocatalysis was involved. Copp, *et al.*,[14] found that, in the "hot spot" decomposition of PETN and RDX at about 700° which they observed directly by an ingenious technique, $k'(T)$ was given by

$$k'(T)\ 10^{13}e^{-34{,}500/RT} \text{ for RDX}$$

and

$$k'(T)\ 10^{12}\ e^{-28{,}400/RT} \text{ for PETN}$$

giving values of about 10^{10} and 10^9 for A' and entropies of activation of -1.4 and -6.0 e.u., respectively. These data were obtained in observed first-order decomposition and are thus apparently representative of the true absolute reaction rates for these explosives. Autocatalysis must, of course, disappear at very high temperatures because the autocatalyst cannot then form.

The above considerations suggest that in the region of true first-order decomposition ΔS^* varies from about -1 to -8 e.u. for the CHNO explosives so far considered. Since the initial rate of decomposition of the pure explosives most nearly satisfies the first-order law one might, therefore, simply assign arbitrarily an average entropy of activation of say -3.2 e.u. to agree with results for TNT, AN and HMN, and compute ΔH^* from the observed decomposition rate in cases where autocatalysis is involved over all measurable parts of the decomposition curve such that one cannot obtain the true first-order decomposition directly. On the basis of this assumption which gives $A' = 10^{9.6}$, the values of ΔH^* computed from the data of ref. 10 were 33.3 kcal./mole for tetryl and 31.7 kcal./mole for PETN. Robertson's[13] data for RDX on the basis of an assumed $A' = 10^{9.6}$ give $\Delta H^* = 33.3$ kcal./mole. These results are in substantial agreement with those of Copp, *et al.*[14]

Now in assigning a detonation temperature we have made use of what may be considered an *upper limit* detonation temperature and a *lower limit* one. For the former, the variable covolume equation of state

$$pv = nRT + \alpha(v)p \qquad (5)$$

was used obtaining the solution for T_2 by means of the "inverse method," *i.e.*, experimental $D(\rho_1)$ data were used to determine $\alpha(v)$ through the hydrodynamic theory. As a lower limit detonation temperature calculations by the Kistiakowsky, Wilson and Brinkley equation of state

$$pv = nRT\ (1 + xe^x) \qquad (6)$$

were used where $x = K/T^{+1/4}v$. For low density explosives the various equations of state used in detonation studies give results not greatly different; the difference between different equations of state becomes much more pronounced at high densities.[15] In this study intermediate to low densities were employed and the differences in T_2 by equations 5 and 6 were quite large only for RDX (5400°K. by equation 5 and 3700°K. by equation 6).

Table V gives comparisons between $k'(T)$ data, computed from Equation 4 for detonation temperatures (T_2) determined by use of equations of state (5) and (6), and the hydrodynamic theory data being taken from ref. 15, Fig. 7 for EDNA and Table III, ref. 16 for PETN, RDX, Tetryl and TNT, and from reference 6 for AN. The k' (detonation) given in Table V were determined from applications of the Eyring erosion model (equation 3) in the nozzle, curved front and geometrical models employing the observed $D(d)$ curves of this investigation to evaluate τ in each theory and equation 3 to evaluate k'. Comparisons for TNT and AN from ref. 3 and 6 are also included.

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TABLE V

COMPARISONS OF k' (THERMAL) WITH k' (DETONATION)

Explosive	Density (g./cm.^{3})	Temp. T_2(°K.)	log A'	ΔH^* (kcal./mole)	log $k'(T_2)$ (Thermal)	log $k'(T_2)$(Detonation)		
						Nozzle	Curved front	Geometrical
PETN	0.95	5350[a]	9.0[14]	28.4[14]	11.57	12.2	12.6	11.3
		4130[b]			11.12			
RDX	1.2	5400[a]	10.0[14]	34.5[14]	12.28	12.2	12.7	11.3
		3700[b]			11.57			
Tetryl	0.95	4200[a]	(9.6)[c]	33.3[c]	11.49	12.0	..	11.1
		3620[b]			11.16			
EDNA	1.0	4070[d]	8.5[10]	30.8[10]	10.47	11.7	12.1	10.9
		3300[e]			10.02			
TNT[3]	0.8 to 1.0	3600[a]	9.47[10]	43.4[10]	10.43	11.8	12.2	10.8
			8.70[17]	34.4[17]	10.13			
		3170[b]	9.47	43.4	10.00			
			8.70	34.4	9.86			
AN	1.0	1720[a]	9.57[10]	38.3[10]	7.89	9.5	9.6	8.04

[a] From ref. 16 for covolume equation of state (5). [b] From ref. 16 for KWB equation of state (6). [c] From rate of decomposition data of ref. 10 assuming $\Delta H^* = 32$ e.u. [d] From Fig. 7, ref. 15 for $c = 0$ and velocity equation 2. [e] From Fig. 7, ref. 15 for $c = -1/4$ and velocity equation 2.

The critical factor in the extrapolation by equation 4 from low temperature thermal decomposition results to detonation temperatures involves the frequency factor A'. Errors in ΔH^* are much less critical in such an extrapolation; they would, however, become very critical if the reverse extrapolation were used with the comparable experimental errors in $\Delta H^*/R'T$ determined at high temperatures. That is, errors in ΔH^* determined at high temperatures would be greatly exaggerated in extrapolations from high to low temperatures *via* equation 4, but errors in ΔH^* determined at low temperatures are diminished in importance in extrapolations to high temperatures. If the mechanism remains unchanged, *i.e.*, if the same reaction mechanism is involved in thermal decomposition as in detonation, the extrapolation used here should, therefore, be entirely reliable. The Eyring surface erosion model implies that the detonation reaction involves (surface) thermal decomposition, and it is thus perhaps not surprising that the extrapolated values should agree as to order of magnitude with the k' (detonation) values determined by the various theories. The evidence in Table I that the geometrical model generally gives k' values in better agreement with the $k'(T)$ extrapolated from thermal decomposition data by means of equation 4 must, of course, be considered in terms of a possible change in reaction mechanism over such a large extrapolation. The evidence, however, is that no change actually occurs except for the mechanical limitation in detonation that causes a pseudo two-thirds order reaction by limiting the true first-order reaction to surface molecules only. This difference, however, does not come into consideration in comparisons of the absolute reaction rate constants which turn out to be fundamentally the same. It does appear, therefore, that the geometrical model affords a rather satisfactory over-all correlation, usually giving even better than mere order-of-magnitude agreement with thermal decomposition data extrapolated by means of the Eyring absolute reaction rate theory.

Aside from this excellent correlation between the extrapolated thermal decomposition and the detonation k's, we mention finally that direct pressure–time measurements for TNT and AN in TNT by the "Cannon" method supported the relatively longer reaction times of the geometrical model[18,19] as compared with those of the nozzle and curved front theories.

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