X-ray data were obtained on 0, 20, 50, 80, and 100% mixes of each system in 1-mm. borosilicate glass capillaries. An XRD unit (General Electric Co.) with nickel-filtered Cu$K\alpha$ radiation was used with 0.025-inch pinhole system and a sample-to-film-distance of 5 or 10 cm. After melting, cooling (and storage), patterns were taken at appropriate temperatures as indicated in Table III.

It is clear from thermal and diffraction data for all three systems, EP-ES, MP-MS, and ES-MS, that there is an intermediate composition region of stable α form at the melting point. At lower temperatures, the α form gives way to tilted forms. In the ES-MS case, as well as in the others, the stable α region is obviously a region of solid solution of ES and MS in the α form, although ES and MS are different in polymorphic behavior.

From the melting level, it may be inferred that the form from melt obtained for pure MS is the lower-melting polymorph. Presumably, there is a real phase difference not revealed by powder data, although indicated by more powerful technique (*1*).

The first order spacings are not easily observed for mixed methyl esters, but presumably they indicate double-chain length structures. There remains the problem of apparent solid solution in the non-alpha states in the ES-MS system when ES crystals are single-chain length and MS are double (or quadruple).

LITERATURE CITED

(1) Aleby, S., von Sydow, E., *Acta Cryst.* **13**, 487-92 (1960).
(2) Francis, F., Piper, S.H., *J. Am. Chem. Soc.* **61**, 577-81 (1939).
(3) Guy, J.B., Smith, J.C., *J. Chem. Soc.* **1939**, 615-18.
(4) Lutton, E.S., Jackson, F.L., Quimby, O.T., *J. Am. Chem. Soc.* **70**, 2441-5 (1948).
(5) Malkin, T., *J. Chem. Soc.* **1931**, 2795-805.
(6) Smith, J.C., *Ibid.*, **1931**, 802-7.

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Formation of Gaseous Detonation Waves

A Comparison of the Knallgas-Steam and Heavy Knallgas–Heavy Water Mixtures

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DETONATION in saturated knallgas ($2H_2 + O_2$)-steam mixtures has been investigated very completely. The effects of mode of ignition, reactor diameter, reactor length, and initial mixture density on the formation of detonation were previously considered and reported (*1, 6*). Since deuterium oxide (heavy water) is often used in atomic reactors, the heavy knallgas ($2D_2 + O_2$)-heavy water system has also been studied. The experimental procedure and the method of analysis and interpretation of these data were identical to those for the knallgas-steam mixtures (*6*). Presented are data for the formation of detonation in the heavy knallgas–heavy water system at 100° C. utilizing spark ignition (360 millijoules) in a 1-inch i.d. reactor of 13-foot length. Comparisons of these data to knallgas-steam data at identical conditions are presented.

RESULTS AND DISCUSSION

Figures 1 and 2 present the results of this study. From them comparisons may be drawn between the knallgas-steam and the heavy knallgas–heavy water media. In Figure 1 ideal detonation parameters of heavy knallgas-heavy water (*7*) from Table I are included for comparison with the measured reaction properties. The theoretical reflected detonation pressures for heavy knallgas–heavy water (Figure 1) were only approximately 10% lower than those for the knallgas-steam system while the measured reaction properties for the two systems differed markedly. In the predetonation region, reaction pressures for the heavy hydrogen system were significantly lower than those for the knallgas-steam system at comparable conditions and composition. Reaction characteristics of these mixtures indicates that the no reaction limit was 19 mole % heavy knallgas for the former mixture as compared to 6 mole % knallgas for the latter mixture. In a richer initial composition region (Figure 1), the transition from a combustion type mechanism of reaction to a shock-propagated reaction occurred at a much higher composition for the heavy hydrogen system. The induction composition [first intersection of measured and theoretical curves (*6*)] was 62 mole % heavy knallgas and 48 mole % knallgas, respectively.

In addition, knallgas-steam showed a much broader region of mixture compositions between the induction composition and the point the measured curve recrossed the theoretical detonation curve, signifying stable wave formation (*6*). Stable detonation waves occurred at 67 mole % knallgas and 72 mole % heavy knallgas.

In Figure 2, where percentage of combustible-reacted curve is plotted *vs.* the initial mixture composition, an abrupt rise in percentage of reacted curves occurred at approximately 53 mole % heavy knallgas and 45 mole % knallgas. These data substantiate the fact that shock-propagated reactions are more difficult to form in the heavy hydrogen system.

The marked differences which occurred in the explosive range might be explained by the fact that the kinetics of the deuterium-oxygen reaction is slower than the hydrogen-oxygen reaction (*3-5*). Experimental and theoretical properties of dry knallgas and heavy knallgas were compared recently (*2*). Even though the measured stable detonation pressures for heavy knallgas as reported by this investigation were subideal at low pressures (less than 2 to 3 atm.), in general the two dry hydrogen systems did not show the significant differences as reported for the two saturated systems. The heavy knallgas-heavy water system exhibits: a higher no-reaction limit, much lower pressure in the predetonation region, a higher induction

Table I. Calculated "Ideal" Detonation Properties of Heavy Knallgas Saturated with Heavy Water at 373.16° K. (7)

					Equilibrium Wave Composition, Mole Fraction					
P_1	X_{hk}	T_2	P_2	D	y_a	y_b	y_c	y_d	y_e	y_f
(Incident Wave Parameters)										
1.5	0.3617	2216	14.03	1837	0.9770	0.0142	0.0066	0.0021	0.0001	0.0001
2.0	0.5198	2701	22.16	2074	0.8965	0.0613	0.0267	0.0137	0.0005	0.0013
3.0	0.6787	3096	37.25	2280	0.7792	0.1267	0.0515	0.0353	0.0021	0.0061
4.0	0.7584	3292	52.13	2386	0.7155	0.1590	0.0630	0.0488	0.0034	0.0103
5.0	0.8064	3418	67.16	2454	0.6773	0.1783	0.0691	0.0575	0.0043	0.0134
7.5	0.8705	3608	104.98	2551	0.6284	0.2021	0.0759	0.0690	0.0056	0.0180
10.0	0.9026	3720	143.12	2606	0.6062	0.2124	0.0785	0.0764	0.0062	0.0203
12.5	0.9218	3798	181.39	2641	0.5941	0.2178	0.0796	0.0803	0.0065	0.0216
15.0	0.9347	3858	219.85	2667	0.5875	0.2206	0.0801	0.0829	0.0066	0.0223

				Equilibrium Wave Composition, Mole Fraction					
P_1	X_{hk}	T_3	P_3	y_a	y_b	y_c	y_d	y_e	y_f
(Reflected Wave Parameters)									
1.5	0.3617	2467	32.46	0.9550	0.0273	0.0123	0.0051	0.0001	0.0003
2.0	0.5198	2947	51.73	0.8538	0.0848	0.0358	0.0221	0.0009	0.0026
3.0	0.6787	3358	87.62	0.7261	0.1528	0.0604	0.0500	0.0030	0.0093
4.0	0.7584	3571	122.79	0.6597	0.1862	0.0711	0.0638	0.0046	0.0148
5.0	0.8064	3708	158.42	0.6217	0.2046	0.0761	0.0734	0.0056	0.0185
7.5	0.8705	3925	248.32	0.5711	0.2282	0.0819	0.0874	0.0072	0.0243
10.0	0.9026	4054	338.96	0.5484	0.2382	0.0939	0.0945	0.0078	0.0271
12.5	0.9218	4146	429.96	0.5367	0.2432	0.0846	0.0988	0.0081	0.0285
15.0	0.9347	4215	521.65	0.5299	0.2459	0.0849	0.1017	0.0083	0.0294

D = stable detonation velocity, meters/second
P = pressure, atm.
T = temperature, ° K.
X = mole fraction, initial mixture composition
y = mole fraction, equilibrium composition
1 = initial gas condition
2 = stable incident detonation
3 = stable reflected detonation
a = D_2O
b = D_2
c = O_2
d = OD
e = D
f = O
hk = heavy knallgas ($2D_2 + O_2$)

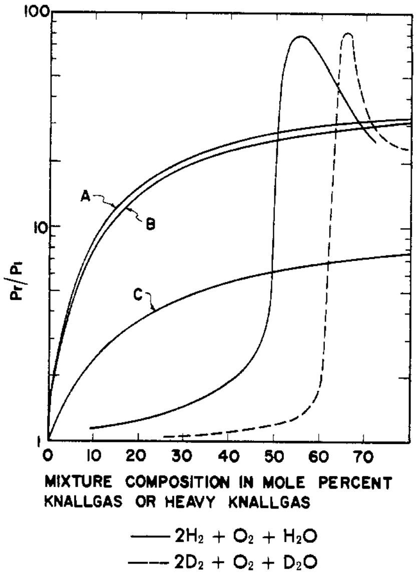

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Figure 1. Comparison of reaction pressure of knallgas-steam to heavy knallgas–heavy water mixtures

A. Theoretical reflected detonation ($2H_2 + O_2 + H_2O$)
B. Theoretical reflected detonation ($2D_2 + O_2 + D_2O$)
C. Theoretical explosion ($2H_2 + O_2 + H_2O$)

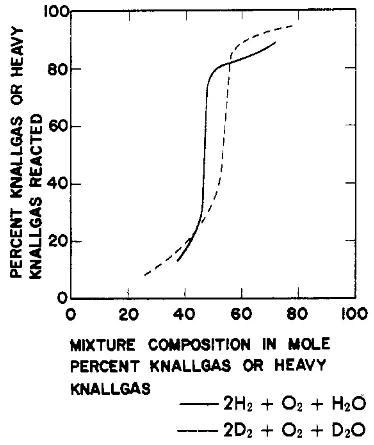

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Figure 2. Comparison of per cent of combustible-reacted for knallgas–steam and heavy knallgas–heavy water mixtures

composition, a much narrower overpressure region, and a higher composition to form a stable detonation wave than the knallgas-steam system at comparable conditions. These facts indicate that a strong internal inhibiting effect is controlling or at least prevailing for this gaseous mixture.

CONCLUSIONS

Formation of detonation in the heavy knallgas-heavy water system differs markedly from formation of detonation in the knallgas-steam system at comparable conditions. These differences cannot be accounted for by the relative reaction rates of deuterium and oxygen as compared to hydrogen and oxygen. The data seem to indicate that heavy water acts not only as a diluent but as a more active inhibitor than steam. Further work on these systems is merited to attempt to explain this phenomenon.

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LITERATURE CITED

(1) Adler, L.B., Hobaica, E.C., Luker, J.A., *Combustion and Flame* **3**, 481 (1959).
(2) Adler, L.B., Luker, J.A., Ryan, E.A., J. CHEM. ENG. DATA **6**, 256 (1961).
(3) Buckler, E.J., Norrish, R.G.W., *Proc. Roy. Soc. (London)* **A147**, 48 (1934).
(4) Chesick, J.P., Kistiakowsky, G.B., *J. Chem. Phys.* **28**, 956 (1958).
(5) Hinshelwood, C.N., Williamson, A.T., Wolfenden, J.H., *Proc. Roy. Soc. (London)* **A167**, 318 (1938).
(6) Luker, J.A., Hobaica, E.C., J. CHEM. ENG. DATA **6**, 253 (1961).
(7) Ryan, E.A., M.S. thesis, Syracuse Univ., Syracuse, N. Y.

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