XXXVII.—*The Inflammation of Mixtures of the Olefins and Air in a Closed Spherical Vessel.*

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PARALLEL experiments to those already described (J., 1927, 2069) on the inflammation of mixtures of the paraffins and air have been made with ethylene, propylene, and butylene. The mixtures, initially at atmospheric pressure and room temperature (about 17°), were ignited by a secondary discharge at the centre of a closed spherical vessel of bronze, of 4 litres capacity, having its interior highly polished. Records of the pressures developed and their rates of development were obtained, and the results are summarised in the following tables, the term " molecular ratio " denoting the ratio of the number of molecules in unit volume at the moment of maximum temperature to the initial number.

TABLE I.

Mixtures of Ethylene and Air.

Theoretical mixture for complete combustion: 6·53% C_2H_4.
Approximate limits of inflammability: 3·4—16% C_2H_4.

Ethylene, %.	Time from ignition to first indication of press. (sec.).	Time from ignition to maximum press. (sec.).	Maximum press. above atmospheric (atm.).
4·14	0·042	0·092	5·58
4·45	0·035	0·070	6·29
4·86	0·027	0·051	6·74
5·07	0·022	0·044	6·67
5·10	0·020	0·040	6·80
6·18	0·012	0·029	7·71
6·60	0·009	0·0265	7·70
6·82	0·010	0·027	7·91
7·57	0·010	0·028	7·96
7·94	0·013	0·029	7·96
8·04	0·014	0·030	8·12
8·20	0·013	0·027	8·12
9·50	0·020	0·050	7·76
10·36	0·026	0·068	7·45

Calculated Maximum Temperatures and Pressures.

C_2H_4, %.	Products of combustion at moment of maximum temperature, %.						"Molecular ratio."	Maximum temp.	Press. rise, atm.
	CO_2.	CO.	H_2O.	H_2.	O_2.	N_2.			
6	8·64	2·97	12·81	0·43	3·30	71·85	1·0173	2437°	8·56
7	7·72	5·65	14·13	0·82	1·74	69·94	1·0333	2530	9·07
7·5	7·22	6·92	14·64	1·13	1·05	69·04	1·0420	2555	9·24
8	6·42	8·50	14·98	1·58	0·62	67·90	1·0531	2560	9·37
9	4·60	11·79	14·97	2·99	0·12	65·53	1·0798	2505	9·40
10	3·19	14·52	13·94	5·31	0·02	63·02	1·1101	2415	9·29

TABLE II.

Mixtures of Propylene and Air.

Theoretical mixture for complete combustion: 4·44% C_3H_6.
Approximate limits of inflammability: 2—8% C_3H_6.

Propylene, %.	Time from ignition to first indication of press. (sec.).	Time from ignition to maximum press. (sec.).	Maximum press. above atmospheric (atm.).
3·18	0·059	0·098	5·69
3·22	0·057	0·096	5·92
3·40	0·049	0·080	6·32
3·42	0·032	0·078	6·70
3·50	0·033	0·068	6·79
3·82	0·023	0·060	7·20
4·28	0·027	0·049	7·12
4·64	0·023	0·044	7·48
4·89	0·023	0·040	7·54
5·45	0·024	0·043	7·65
5·67	0·026	0·046	7·66
6·06	0·035	0·059	7·47
6·58	0·053	0·101	7·35
6·89	0·056	0·113	7·05
7·54	0·102	0·256	5·68
7·65	0·115	0·380	5·18
7·84	0·153	0·470	4·40

TABLE II (*contd.*).

Calculated Maximum Temperatures and Pressures.

C_3H_8, %.	Products of combustion at moment of maximum temperature, %.						"Molecular ratio."	Maximum temp.	Press. rise, atm.
	CO_2.	CO.	H_2O.	H_2.	O_2.	N_2.			
3·5	9·11	0·97	11·63	0·13	4·78	73·28	1·0228	2235°	7·90
4·5	9·00	3·69	13·83	0·48	1·84	71·16	1·0439	2445	8·85
4·8	8·37	5·06	14·28	0·76	1·33	70·20	1·0543	2460	9·00
5·1	7·82	6·30	14·76	1·00	0·76	69·36	1·0640	2467	9·13
5·8	6·09	9·56	14·99	2·22	0·13	67·01	1·0929	2425	9·24
6·5	4·23	12·78	14·34	4·17	0·01	64·47	1·1274	2315	9·12
7·0	3·28	14·63	13·46	5·94	Trace	62·69	1·1529	2217	8·98

TABLE III.

Mixtures of Butylene and Air.

Theoretical mixture for complete combustion : 3·37% C_4H_8.
Approximate limits of inflammability : 2—6% C_4H_8.

C_4H_8, %.	Time from ignition to first indication of press. (sec.).	Time from ignition to maximum press. (sec.).	Maximum press. above atmospheric (atm.).
2·14	0·091	0·193	5·30
2·39	0·063	0·107	5·84
2·58	0·040	0·088	6·40
3·07	0·027	0·056	7·34
3·65	0·021	0·045	7·95
4·07	0·019	0·041	8·03
4·23	0·020	0·042	7·94
4·44	0·023	0·046	7·82
4·53	0·023	0·048	7·95
4·65	0·026	0·056	7·96
5·21	0·040	0·087	7·65
5·27	0·048	0·094	7·38
5·84	0·073	0·181	6·75
6·53	0·128	0·564	4·54

Calculated Maximum Temperatures and Pressures.

C_4H_8, %.	Products of combustion at moment of maximum temperature, %.						"Molecular ratio."	Maximum temp.	Press. rise, atm.
	CO_2.	CO.	H_2O.	H_2.	O_2.	N_2.			
3·0	9·36	1·99	12·73	0·26	3·26	72·40	1·0412	2337°	8·45
3·5	8·80	4·20	14·00	0·60	1·65	70·75	1·0598	2430	8·94
3·85	8·05	6·05	14·75	0·94	0·73	69·48	1·0755	2455	9·19
4·2	6·87	8·22	15·05	1·59	0·25	68·02	1·0950	2435	9·29
5·0	4·08	13·01	14·27	4·30	0·01	64·33	1·1486	2272	9·15

The Pressures developed.—In Fig. 1 a graphical comparison is made of the variation of maximum pressure, both calculated and observed, with composition of the mixtures. In Table IV are given data, obtained from Fig. 1, comparing the observed and the calculated maximum pressures and recording the amounts of "lost pressure" expressed as percentages of the calculated values. The theoretical mixtures for complete combustion are recorded in the first column of the table. As with the paraffins, there is with each olefin a marked "displacement" of the observed maximum-pressure mixture, from the theoretical mixture for complete combustion, towards excess of hydrocarbon. These displacements can only be attributed to the effects of dissociation, since the calculated values, for which an allowance is made for dissociation, are similarly displaced.

FIG. 1.

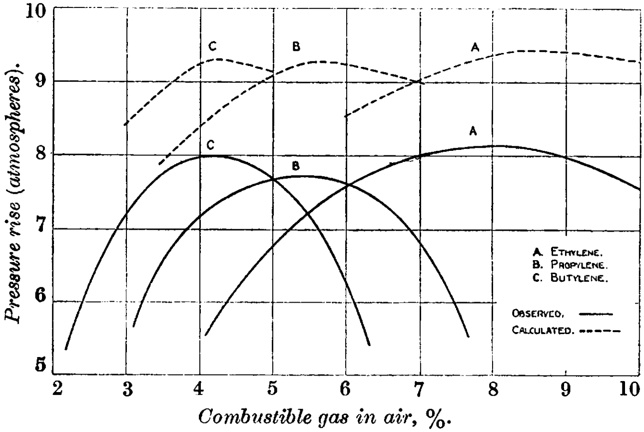


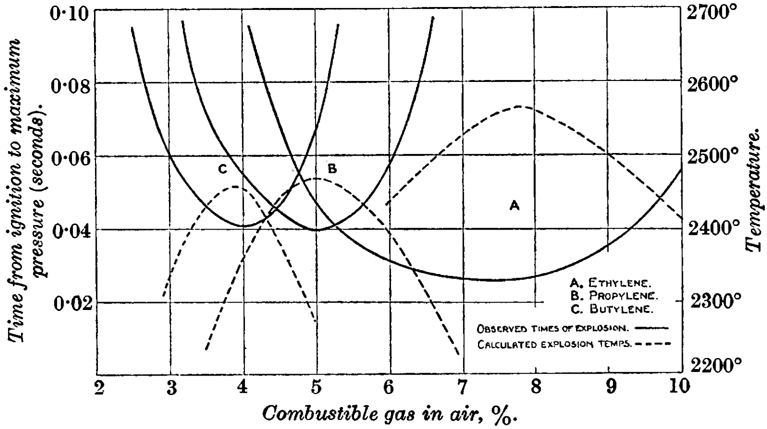
TABLE IV.

	Theoretical mixture for complete combustion, %.	Mixture giving maximum press., %.		Maximum press., atm.		Lost press., %.
		Calc.	Obs.	Calc.	Obs.	
C_2H_4 ...	6·53	8·35	8·25	9·42	8·15	13·6
C_3H_6 ...	4·44	5·50	5·45	9·28	7·75	16·5
C_4H_8 ...	3·37	4·20	4·20	9·30	8·00	14·0

The "lost pressures" are greater than were calculated for the paraffins, for which the highest value, with methane, was 9·8%. Whilst this result may be due to errors in the data used in the calculations, it is possible that the loss of heat during explosion of the olefins is higher than with the paraffins, either through greater radiation or by reason of less complete combustion at the moment of maximum pressure. As regards possible errors in the data, we have previously pointed out that Bjerrum's values for the mean specific heats of steam are probably too low over the temperature range concerned (*loc. cit.*; and J., 1928, 15). There is no reason to believe, however, that the error thus introduced into the calculations would be more marked at the somewhat higher temperatures attained on explosion of olefin–air mixtures, for Bjerrum's values increase rapidly with temperature over this range (2000—3000°).

On the other hand, it does not seem probable that conduction losses can materially affect the pressures attained under the conditions of experiment, except with mixtures near the limits of inflammability (in which flame does not spread spherically from the point of ignition) or with such mixtures as exhibit considerable "after-burning." None of the time–pressure records with the olefin–air mixtures showed the flattened crest, or initial retardation of the cooling curve, usually associated with "after-burning." On the whole, higher radiation losses, due to the higher explosion-temperatures attained, would seem to be the most reasonable explanation of the greater "lost pressures."

FIG. 2.



The Rate of Development of Pressure.—Fig. 2 shows the effect of composition of the mixtures on the "time of explosion" (the interval between ignition and the attainment of maximum pressure) and on the (calculated) explosion-temperatures. Table V, compiled from Fig. 2, makes comparison between the observed "maximum-speed" mixtures and the calculated "maximum-temperature" mixtures. The "maximum-speed" mixture for each gas is that for which the "time of explosion" is least.

TABLE V.

Composition of Maximum-speed and Maximum-temperature Mixtures

	Olefin in max.-speed mixture (obs.), %.	Olefin in max.-temp. mixture (calc.), %.	Mean temp., calc.	Time (obs.) from ignition to maximum pressure (sec.).
C_2H_4	7·6	7·8	2563°	0·026
C_3H_6	5·0	5·0	2468	0·040
C_4H_8	4·0	3·9	2457	0·041

As with the paraffins (*loc. cit.*), the close correspondence between the observed values for the maximum-speed mixtures and the calculated values for the maximum-temperature mixtures shows that, for mixtures of a given combustible gas with air, flame temperature is the controlling factor in determining the mean rate of development of pressure. From recent experiments by Miss E. M. Georgeson and Mr. F. J. Hartwell (private communication), it is evident that the speed of the uniform movement of flame in mixtures of the olefins with air is also controlled mainly by the flame temperature, for the compositions of the maximum-speed mixtures (see Table VI) are the same as in our experiments. The order of speed of the flames is also the same.

TABLE VI.

Uniform Movement in Olefin–Air Mixtures.

(Georgeson and Hartwell.)

	Olefin in maximum-speed mixture (obs.), %.	Speed (cm./sec.) of uniform movement (obs.) (2·5-cm. diam. tube).
Ethylene ...	7·6	165
Propylene ...	5·1	101
Butylene ...	4·0	98

The displacement of the maximum-temperature mixture from that for complete combustion towards excess of inflammable gas, deduced by Tizard and Pye (Empire Motor Fuels Committee, Report, 1923—24) and by ourselves, has recently been observed experimentally by Loomis and Perrott (*Ind. Eng. Chem.*, 1928, **20**, 1004), who find that the methane–air and propane–air mixtures giving the highest flame temperatures contain 9·8% of methane and 4·2% of propane. Our calculated values (*loc. cit.*, p. 2078) were 10·0% and 4·4% respectively; whilst the mixtures for complete combustion contain 9·47% and 4·0%, respectively.

EXPERIMENTAL.

The apparatus and mode of procedure were as for the experiments on the inflammation of mixtures of the paraffins and air (see also J., 1918, **113**, 844). The gases were obtained commercially and purified by liquefaction and fractional distillation until the theoretical values for the ratio C/A were obtained on explosion analysis (C = contraction; A = subsequent absorption by potassium hydroxide solution). The butylene consisted of normal and *iso*-hydrocarbons in nearly equal proportion.

Calculations.—The method of calculation of maximum temperatures and pressures, and the data used were as for the paraffins, with the following additional data for heats of combustion (lower values) at constant volume: Ethylene 325·3, propylene 462·3, butylene 610·2 kg.-cals. per g.-mol.

Note.—In our paper on the pressures produced on inflammation of mixtures of carbon monoxide and air (J., 1928, 17), the following correction should be made with respect to the dissociation of carbon dioxide: "Expressed as percentages, the corresponding values at 1 atm. and 2543° K are: Fenning and Tizard, 13·8; Bjerrum, 20·7; Maxwell and Wheeler, 25·6." The correction in no way affects the argument advanced in the paper.

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