the covalent radii, which is 2.47 Å. The radius sum for ions would be 3.22 Å.[24]

Summary

1. From a consideration of the peculiarities of Eder's reaction the hypothesis has been developed that the chain carriers are the half-oxidized oxalate ion and the unpolymerized mercurous ion Hg^+.

2. Additional evidence for the formation of an active reducing agent by oxidation of oxalates has been presented.

3. Mercury has been shown to be present in the calomel formed in Eder's reaction under favorable conditions.

4. It has been shown that the reaction may be induced by addition of reducing agents.

5. Calculations have been made which indicate that the normal potential of the half-reaction $Hg(l) \rightleftarrows Hg^+ (aq) + \epsilon$ should be -1.71 volts.

6. This potential has been combined with other mercury potentials to show that the dissociation of the ordinary mercurous ion Hg_2^{++} in solution is attended by a standard free-energy change of 42 kcal.

BUFFALO, N. Y. RECEIVED DECEMBER 11, 1940

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[24] After the manuscript of the present paper had been almost completed, the November issue of THIS JOURNAL was received, in which Kolthoff and Barnum (**62**, 3061 (1940)) suggest that their data on the anodic behavior of cysteine can be explained only by the assumption of an unpolymerized mercurous salt HgSR. They point out that at extremely low concentrations the Hg_2^{++} ion may be considerably dissociated. From equation (3) above, the equilibrium constant for the reaction $Hg_2^{++} \rightleftarrows 2Hg^+$ is found to be 10^{-31}. Taking 10^{-18} as the solubility product constant for calomel, it may be calculated that in saturated aqueous calomel the mercurous ion is not dissociated into Hg^+ ions to an appreciable extent. The dissociation would be greater at the extremely low concentrations prevailing in the work of Kolthoff and Barnum, but could hardly account for their results except for the strong affinity of mercury for sulfur and possible specific effects of the cysteine radical.

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Kinetics of Oxidation of Typical Hydrocarbons

BY R. A. DAY, JR., AND R. N. PEASE

It is generally agreed that the tendency of a hydrocarbon to knock when used as a fuel in an internal combustion engine is related in some way to the ease with which the fuel–air mixture undergoes spontaneous ignition. The experiments of Townend and his co-workers[1] with regard to the influence of pressure on the temperature required for spontaneous ignition showed the existence of a tongue, or peninsula, in a pressure–temperature plot of the ignition curve, pointing toward lower pressures at temperatures around 300–350°. Such peninsulas are generally bounded on the low pressure side by a region in which mild explosions, or so-called "cool flames" are observed, and the peninsula and cool flame regions are usually termed the "low temperature system." A comparison of the ignition curves of branched chain paraffins with those of their straight chain isomers revealed that higher temperatures and pressures are required over the whole range in order to effect the ignition of the former. This is in accord with the well-known tendency of branched chain compounds to resist knock when used as fuels.

A further comparison has now been made of the ignition and cool flame characteristics of some highly branched paraffins, and the study was extended to include two naphthenes and also benzene. The compounds studied were *n*-heptane, 2,2,3-trimethylbutane, 2,2,4-trimethylpentane (iso-octane), 2,2,3,3-tetramethylbutane (hexamethylethane), benzene, cyclohexane, cyclopropane, and propane. A few runs were also made with propylene, propylene oxide and ethylene oxide. Use was made of oxygen instead of air to effect combustion, so that cool flame formation and ignition occurred well below atmospheric pressure. In the slow combustion region the rates of oxidation could be measured conveniently by pressure change, and permitted a further comparison of these compounds.

Experimental Procedure

The experiments were conducted in a static apparatus previously described.[2] The only modification necessary in the case of liquid hydrocarbons was the use of Pyrex-plug stopcocks which were wound with chromel wire and heated electrically to prevent condensation. A high-temperature stopcock grease made from finely powdered bentonite and

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[1] Townend and Mandlekar, *Proc. Roy. Soc.* (London), **A141**, 484 (1933); **A143**, 168 (1933); Townend, Cohen and Mandelkar, *ibid.*, **A146**, 113 (1934); Townend and Chamberlain, *ibid.*, **A154**, 95 (1936); Maccormac and Townend, *J. Chem. Soc.*, 238 (1938).

[2] Day and Pease, THIS JOURNAL, **62**, 2234 (1940); see also Newitt and Thornes, *J. Chem. Soc.*, 1656 (1937).

glycerol[3] was employed and found to be satisfactory.

The two gases, propane, and cyclopropane, were commercial products and were used without further purification. The normal heptane after purification had the following properties: n^{20}_{D} 1.38769; specific gravity 0.6836^{20}_{4}; b. p. 98.41° at 760 mm. of mercury. (Tests for sulfur were negative and the iodine value was zero.) The cyclohexane had the following properties: n^{20}_{D}, 1.4258; specific gravity 0.7786^{20}_{4}; b. p. 81.1° at 760 mm. of mercury and the iodine value was zero. The three compounds 2,2,4-trimethylpentane, hexamethylethane, and 2,2,3-trimethylbutane were pure products presented to us by the Ethyl Gasoline Corporation to whom we owe our best thanks. The first two were used without further purification. The trimethylbutane was fractionally crystallized to yield a fraction with d^{20}_{4} 0.6912 and a melting point of about −35°. This fraction still contained some volatile impurity which was removed after a few runs had been made. Reproducible results could then be obtained. The benzene used was the thiophene-free product which had been washed with sulfuric acid and water, dried and distilled from sodium, and finally recrystallized.

The reaction bulb was made of Pyrex glass and was washed before use with hot concentrated nitric acid. It had an inside diameter of 3.5 cm. and a volume of 170 cc. Frequently, after a series of ignitions was run, the bulb became coated with carbon and had to be cleaned again with nitric acid in order to obtain reproducible results.

Observations as to the occurrence of slow reaction, cool flames, or ignition could be made by means of readings of the manometer, or by watching the reaction bulb itself through a glass window in the furnace. Runs were made with each compound at series of constant temperatures, the total pressure being increased by 20 or 30 mm. increments. In this manner boundary points were found where at the lower pressure, for example, slow reaction occurred and at the higher pressure a cool flame was formed. The boundary beyond which the true yellow ignition flame was formed and below which either slow reaction or cool flames occurred was likewise determined. The procedure was to admit the hydrocarbon vapor to the desired pressure first and then oxygen. In the experiments to determine the cool flame and ignition limits the hydrocarbon/oxygen ratio used was 1/3, except in the cases of propane and cyclopropane, where it was 1/1.

For the rate measurements runs were made with hydrocarbon/oxygen ratios of 1/1, 1/3 and 3/1, the total initial pressure being 200 mm. in the first case and 400 mm. in the last two. Most of the runs were made at 270, 320 or 370°, but since these temperatures are above the normal reaction zones of heptane and cyclohexane and below that of benzene, runs were made with these compounds at correspondingly lower and higher temperatures.

Results

Ignition Limits.—A fairly complete diagram of ignition limits was obtained for each compound, but lack of space prevents their presentation in full. Instead, the behavior of a 1:3 iso-octane–oxygen mixture (Fig. 1) is taken as a norm, and the various branches of its curve are labelled. Table I gives the temperatures at which these points are reached at the designated total pressures. The point A represents the lower cool flame limit, below which only slow reaction occurs and above which one cool flame is formed; B represents the upper cool flame limit, above which straight reaction again occurs; C and F represent the upper ignition limit beyond which the true yellow ignition flame is formed; and D and E are the lower and upper boundaries of the ignition peninsula, respectively. For example, if one were working at the constant total pressure of 400 mm. with a 1/1 propane–oxygen mixture and the temperature were being raised, below 285° only slow reaction would be observed; but at 285° (Point D) ignition in the lower region would occur and would continue until the point E at 289° was reached. From this point until B was reached at 371°, cool flames would be formed and from B to C at 429° slow reaction again would occur. Then at all temperatures above C ignition would take place at this pressure. All such series of points are listed in Table I in the order in which they are observed as the temperature is increased.

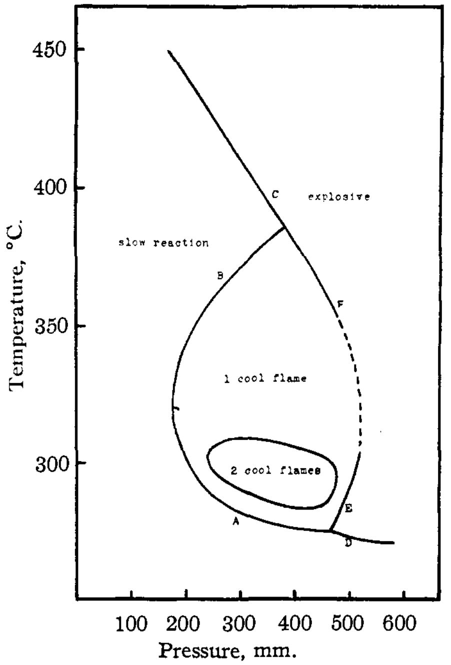

Fig. 1.—Oxidation characteristics of 1:3 iso-octane–oxygen mixtures.

The data are in general similar to those of Townend, *et al.*,[1] for hydrocarbon–air mixtures,

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(3) "Handbook of Chemistry and Physics," 21st edition, Chemical Rubber Publishing Company, Cleveland, Ohio, 1936, p. 1911.

TABLE I

BEHAVIOR OF HYDROCARBON–OXYGEN MIXTURES AT INDICATED TOTAL PRESSURE

Substance	Crit. comp. ratio	Ratio HC/O_2	Total pressure, mm.					
			100	200	300	400	500	600
n-Heptane	2.8	1/3	A-240°					
			C-298°	D-233°	D-230°	D-227°		
Cyclohexane	4.5	1/3	D-269°	D-259°	D-256°			
			E-273°	E-292°				
			F-365°	F-315°				
Iso-octane	7.7	1/3	C-468°	A-302°	A-282°	A-276°	D-273°	D-270°
				B-344°	B-372°		E-291°	
				C-438°	C-408°	C-379°	F-(340°)	
Trimethyl-butane	13.0	1/3	C-478°	C-449°	A-296°	A-284°	A-283°	
					B-346°	B-376°		
					C-422°	C-395°	C-(368°)	
Hexamethylethane	..	1/3	C-483°	C-453°	A-275°	A-270°	A-269°	A-269°
					B-321°	B-344°	B-365°	
					C-426°	C-400°	C-374°	C-(340°)
Propane	12.0	1/1	C-(510°)	A-315°	A-295°	D-285°	D-280°	D-275°
				B-331°	B-355°	E-289°	E-307°	
				C-(483°)	C-456°	B-371°	B-381°	
						C-429°	C-401°	
Cyclopropane	..	1/1		CD-477°	CD-459°	CD-441°	CD-424°	CD-405°
Benzene	15.0	1/3		CD-600°	CD-597°	CD-572°	CD-552°	CD-537°

where comparisons are available. Thus cool flames are observed with *n*-heptane at a lower pressure and temperature than with iso-octane but there is no vast difference. In contrast, benzene gives no cool flames and true ignition is postponed to temperatures over 500°. This is essentially as reported by Maccormac and Townend for mixtures with air, though pressures are then in atmospheres rather than in units of roughly 100–200 mm.

It is also possible to observe a general parallelism with data for the critical compression ratio of the hydrocarbons as fuels in the internal combustion engine (see Table I[4]). The pressure required for ignition at a given temperature increases with the critical compression ratio. However 2,2,3-trimethylbutane seems to be rather out of line.

Only the extraordinary stability of iso-octane observed in the pioneering experiments of Pope, Dykstra and Edgar[5] is rather unexpected. These experiments were carried out with air by the flow method, and showed that whereas *n*-octane reacted freely below 300°, iso-octane was untouched below 500°. It was this difference which first directed attention to the marked advantages of branched-chain paraffins as fuels. The result suggested that iso-octane might be in a class with benzene in its resistance to oxidation. Such is not the case, however. The stability observed in the flow experiments of Pope, Dykstra and Edgar at 1 atmosphere is to be attributed to the fact that the cool flame region for iso-octane–air mixtures is entirely above 2 atmospheres (see Maccormac and Townend[1]). Had the comparison with *n*-octane been made at a higher pressure, no marked difference would have been observed, and the development of fuels containing branched-chain hydrocarbons would have been at least delayed.

It will be noted that cyclopropane does not yield cool flames, but behaves more like methane or benzene, rather than either propane or cyclohexane.

The investigation of hexamethylethane was a matter of some interest because the molecule has neither secondary nor tertiary carbon atoms. Its behavior proved to be very like the isomer, iso-octane (2,2,4-trimethylpentane) which has both. Evidently, the extent of branching rather than the group exposed is the important factor, since hexamethylethane is somewhat less reactive than iso-octane which is otherwise the least reactive of the isomers of octane.

Slow Reaction Rates.—Observations were also made in the range where reaction was slow but measurable. In all cases the rates (in mm. pressure-rise per minute) rose to a maximum and

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[4] Lovell, Campbell and Boyd, *Ind. Eng. Chem.*, **26**, 1105 (1934).

[5] Pope, Dykstra and Edgar, THIS JOURNAL, **51**, 2203 (1929).

TABLE II

RATES OF OXIDATION OF HYDROCARBON–OXYGEN MIXTURES

Approximate initial compositions: Mixture I, 100 mm. H.C., 100 mm. oxygen; Mixture II, 100 mm. H.C., 300 mm. oxygen; Mixture III, 300 mm. H.C., 100 mm. oxygen.

Temp., °C.	200			225			250			270			320			370		
Mixt. no.	I	II	III	I	II	III	I	II	III	I	II	III	I	II	III	I	II	III
	Maximum oxidation rate, mms./min. pressure increase																	
n-Heptane	0.73	0.56	1.8	3.0	3.0	6.0	1CF	Ign.	1CF	1CF	Ign.	1CF	1CF	Ign.	1CF	1CF	Ign.	1CF
Cyclohexane				1.2	1.2	1.9	8.2	Ign.	9.5	1CF	Ign.	1CF	1CF	Ign.	1CF	1CF	Ign.	1CF
Iso-octane				0.4	0.55	2.1	2.3	5.0	6.0	7.0	25	13	20	1CF	1CF	40	114	48
Hexamethylethane										4.3	1CF	5	10	1CF	1CF	21	101	32
Trimethylbutane										1.0	2.6	2.1	8	1CF	1CF	29	96	62
Propane										1.0	1.0	4.2	1CF	6CF	2CF	6.5	56	49
Cyclopropane																0.45	0.45	6.0
Propylene										0.31	0.25	2.0	14	14	2CF	37	80	1CF
Propylene oxide													26			32		
Ethylene oxide													3.5		20	6		

Temp., °C.	500			525			550		
Mixt. no.	I	II	III	I	II	III	I	II	III
Benzene	0.50	4.0	8.1	2.8	22	18	11	70	44

then fell. These maximum rates could be obtained from a plot. They are recorded in Table II.

Somewhat the same qualitative observations could be made about these data as were made about the ignition limits. The order of reactivity remains essentially the same, the list being headed by *n*-heptane and cyclohexane, and so on down.

A few values for propylene, propylene oxide and ethylene oxide have been added for comparison with cyclopropane. All three were found to be decidedly more reactive. It was also shown that the induction period in cyclopropane oxidation could be materially shortened by addition of a little acetaldehyde without markedly changing the subsequent rate.

We were especially interested in making a comparison of *n*-heptane and iso-octane. This proved a little awkward since at higher temperatures the former yielded cool flames, while at lower temperatures the latter gave long induction periods. Nevertheless some data were collected at 225°. These showed iso-octane to react about $^1/_8$ to $^1/_3$ as fast as *n*-heptane. Induction periods were of the order of forty-five and three minutes, respectively. One may also mention that *n*-heptane broke into the rapid-reaction zone just a few degrees higher, whereas iso-octane would support a considerably higher steady rate at higher temperatures without becoming explosive. This simple failure of iso-octane to ignite is of course closely connected with its superiority as a non-knocking fuel. Unfortunately, it is not as yet possible to define the property more precisely in terms of the slow reaction.

Summary

Measurements of cool-flame and ignition regions, and of rates of slow oxidation have been made for a number of hydrocarbon–oxygen mixtures.

Results show that the order of the hydrocarbons is essentially the same in the two series of measurements, and also accords with the order of critical compression ratios in internal combustion engines.

Data relating to hexamethylethane and to cyclopropane are of interest, since no previous work has been reported. Hexamethylethane, in spite of its unique structure, is qualitatively the same as its isomer, iso-octane (2,2,4-trimethylpentane). Cyclopropane proves to be quite resistant to oxidation. Cool flames are not observed. Ignition temperatures are higher and oxidation rates are lower than for either propane or propylene.

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