was made using heat capacity data listed by Kelley.[10] The net result is $\Delta H_{298.16} = -488.8 \pm 0.5$ kcal./mole, which is the heat of formation under standard conditions of tantalum pentoxide from the elements. The assigned uncertainty in this instance (and similarly for the other substances in this paper) takes account of uncertainties in the combustion heat of the metal, calibration of the calorimeter, combustion heat of benzoic acid, completion of combustion and correction for impurities in the metal.

The mean value for niobium corresponds to -453.44 kcal./mole of niobium pentoxide. The corrections to standard state conditions, made in the same manner as for tantalum, yield $\Delta H_{298.16} = -455.2 \pm 0.6$ kcal./mole as the heat of formation of niobium pentoxide from the elements.

The mean value for zirconium is equivalent to -260.82 kcal./mole of zirconium dioxide. Correction to standard conditions results in $\Delta H_{298.16} = -261.5 \pm 0.2$ kcal./mole as the heat of formation of zirconium dioxide.

The mean value for tantalum carbide corresponds to -299.17 kcal. for the reaction

$$TaC + {}^9/_4O_2 = {}^1/_2Ta_2O_5 + CO_2$$

under bomb conditions. Reduction to unit fugacity of oxygen and CO_2 were made jointly, using a suitable modification of Washburn's[9] equation; corrections to a constant-pressure process and to 25° were made as mentioned previously. The result is $\Delta H_{298.16} = -300.0 \pm 0.5$ for the above reaction under standard conditions. Combining with the heats of formation of carbon dioxide[6] and 0.5 mole of tantalum pentoxide leads to $\Delta H_{298.16} = -38.5 \pm 0.6$ kcal./mole as the heat of formation of tantalum carbide from the elements.

Previous heat of formation values of tantalum pentoxide, niobium pentoxide and zirconium dioxide were considered in compiling the N. B. S. Tables,[6] the adopted values being, respectively, -499.9, -463.2 and -258.2 kcal./mole. The present work is considered superior in that purer metals were available for study, the use of a kindler (such as paraffin oil) was avoided, and higher precision was obtained. No value for tantalum carbide is given in the N. B. S. Tables.

Using entropy values listed by Kelley[10] and the assumption that the tantalum and niobium oxides have the same entropy of formation, the following free energies of formation are derived: $\Delta F^\circ_{298.16} = -456.5 \pm 0.6$ kcal./mole for tantalum pentoxide, $\Delta F^\circ_{298.16} = -422.9 \pm 0.7$ kcal./mole for niobium pentoxide, $\Delta F^\circ_{298.16} = -247.7 \pm 0.2$ kcal./mole for zirconium dioxide, and $\Delta F_{298.16} = -38.1 \pm 0.6$ kcal./mole for tantalum carbide.

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(10) K. K. Kelley, U. S. Bur. Mines Bull. 477 (1950).

[CONTRIBUTION FROM MCPHERSON CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

A Chromatographic Study of Carbonyl Compounds Present in a Hydrocarbon–Air Flame[1]

BY EARL W. MALMBERG

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A study has been made of the carbonyl compounds which are present in a hydrocarbon–air flame. The experimental methods included formation and chromatographic separation of the 2,4-dinitrophenylhydrazone derivatives. In addition to the carbonyl compounds which are to be expected in the light of presently accepted mechanisms, a number of synthesis products were obtained, compounds in which the length of the carbon chain was increased. These results are interpreted in terms of the free radicals which must have been present originally, including the formyl radical. Three products, glyoxal, methylglyoxal and formaldehyde were found to be common to eighteen hydrocarbon fuels. Quantitative analyses for these products showed no correlation with the type of fuel. This fact seems to indicate that the differences in the burning characteristics of hydrocarbons lie in the earlier stages of the combustion.

In the study of the mechanism of oxidation of hydrocarbons, the isolation of intermediates is difficult but yields important information as to the nature of the reactions. In the present investigation carbonyl compounds have been isolated from turbulent hydrocarbon–air flames which are quenched by an excess of fuel. A chromatographic study of derivatives of carbonyl compounds was initiated because of the great promise shown by this method for qualitative and quantitative analytical applications. This investigation is in two parts: the development of chromatographic procedures and the application of these methods to the study of flame combustion products.

Development of Chromatographic Methods

The work of Iddles and Jackson[2] has shown that water-soluble carbonyl compounds can be quantitatively precipitated as the 2,4-dinitrophenylhydrazones. At the time our study began Roberts and Green[3] had shown that chromatography on silicic acid adsorbent showed considerable promise. Further study showed that very good separations could be obtained with the derivatives of the lower carbonyl compounds. Gordon[4] and co-workers have since then reported essentially the same separations which were used in the present work. However, the procedures which we developed in-

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(1) This work was presented at the Meeting of the American Chemical Society in Atlantic City, N. J., September, 1952. The work was supported in part by the Air Force Research and Development Command under Contract No. AF 33(038)22959.

(2) H. A. Iddles and C. E. Jackson, *Ind. Eng. Chem., Anal. Ed.*, **6**, 454 (1934).

(3) J. D. Roberts and C. Green, *ibid.*, **18**, 335 (1946).

(4) B. E. Gordon, F. Wopat, H. D. Burnham and L. C. Jones, *Anal. Chem.*, **23**, 1754 (1951).

dependently differ in certain experimental details, and in addition, methods of chromatography of dicarbonyl compounds are reported here. In the initial exploratory work, the chromatographic potentialities of the 2- and 4-nitrophenylhydrazones were investigated. These derivatives were found to be less suitable than the 2,4-dinitro compounds. The ortho compounds were weakly adsorbed and gave less satisfactory separations; the para compounds were unstable in solution with respect to light and atmospheric oxygen. There was also evidence that the para compounds were more prone to engender complications through *cis–trans* isomerism.

Experimental

Materials.—Chromatographic materials and procedures were similar to those already described[5] except that solvents were not redistilled.

Chromatographic Procedures.—All the samples from the turbulent flame showed characteristic chromatograms. Below the predominant band of the formaldehyde and acetaldehyde derivatives appeared the zones of all the simple monocarbonyl compounds (the dinitrophenylhydrazone derivative is meant in all these discussions of chromatographic procedures) with alkyl residue larger than $>CH_2$. Of the zones which appeared above formaldehyde, the bis derivatives of α,β-dicarbonyls were easily characterized by the blue-purple color which they gave with a sodium hydroxide streak reagent on the extruded column. Other more strongly adsorbed zones characteristically appeared in this region; the color with sodium hydroxide and the chromatographic properties indicated complex polycarbonyl character. The percentage of these complex components was in general very low except in the case of products from benzene and cyclopropane. In general an initial separation into these three groups was made by collecting the zones below formaldehyde in the filtrate and obtaining formaldehyde and the dicarbonyls by extrusion and elution of the proper sections.

The practice of extruding the column and noting the positions of the developed zones was used in all final separations. The position of the zone on the interior of the column as well as on the outside can be measured exactly; any errors from distortion can be eliminated. With exact duplication of development the position of the zone of a given compound is duplicated within error of measurement, and thus by reference to the behavior of known compounds with a standard procedure, the column for final isolation could be used as a preliminary identification. The color with sodium hydroxide could be observed. Finally, if distortion of the zone does occur in the interior of the column, the hindrance to separation can usually be obviated in the cutting apart of the extruded column as compared to a flowing chromatogram.

The separations of the lower carbonyl compounds were obtained without difficulty except in the case of the formaldehyde and acetaldehyde derivatives. On the silicic acid adsorbent which was highly satisfactory in other respects, these two compounds always appeared in adjacent positions with no interzone. Early in the work a partition chromatogram between methanol and *n*-heptane was found to give a very good separation but was applicable only to very small samples. Mrs. Jane Bobbitt in this Laboratory has shown that prewashing the column with V_{150} ml. (volume required to wet a column 150 mm. in length) of 10% of acetone in ligroin affords a very fine clear-cut separation of the zones. Care must be taken in other applications of this prewash, however, because double zones may appear under certain conditions.

The extreme insolubility of the bis 2,4-dinitrophenylhydrazones of α,β-dicarbonyl compounds makes chromatographic treatment quite difficult. Mixtures such as 1:15 nitromethane–benzene or 1:15 nitrobenzene–benzene are satisfactory sample solvents for concentrations up to 0.1 mg. per ml. A zone formed from this solvent is not developed by mixtures of ether and ligroin, but satisfactory development is attained with 3% of ether in 1:1 benzene–ligroin. For example, when the osazones of glyoxal, methylglyoxal and dimethylglyoxal were chromatographed with that developer, the respective zones were at 20 to 40, 50 to 80, and 90 to 120, the measurements being in millimeters from the top of the column. The insolubility limits the amount of osazone which can be put on the column and be developed satisfactorily: about 0.1 to 0.3 mg. on a column 14 mm. in diameter is the upper limit. Experiments were made on quantitative recovery of the chromatographed samples; elution of relatively large sample of glyoxal bis-(2,4-dinitrophenylhydrazone) with ethanol gave a recovery of 90%. When smaller samples were eluted with 1:1 acetone–ether the recovery was better because the adsorbent was completely colorless when treated with aqueous sodium hydroxide. This color test is extremely sensitive and is used for the micro-estimation of these osazones.

An α,γ-dicarbonyl compound, acetylacetone, yields a pyrazole when treated with 2,4-dinitrophenylhydrazine in 2 *N* hydrochloric acid.[6] This product is quite soluble and must usually be obtained from the solution by extraction. When chromatographed the pyrazole was found to yield a colorless zone more strongly adsorbed than the formaldehyde hydrazone. The zone was characterized by the alkaline streak reagent; a rose-pink color appears and then fades rapidly.

Quantitative Procedures.—The procedure of analysis for a mixture of the derivatives of glyoxal, methylglyoxal and formaldehyde consisted of dissolving a 3- to 10-mg. sample of the dinitrophenylhydrazone precipitate in 8 drops of nitromethane and 5 ml. of benzene and chromatographing this sample on a 14-mm. column. Development was carried out with enough 10% ether in ligroin to move the formaldehyde derivative into the lower half of the column and then developing and separating the osazones with 3% ether in 1:1 benzene–ligroin. The procedure was standardized so that the positions of the zones served as a qualitative identification. The zones were eluted with ethanol and the concentrations measured spectrophotometrically on a Beckman DU instrument; the absorption maximum and spectrophotometric factor[7] for the dinitrophenylhydrazine derivatives were: glyoxal, 435 mμ and 0.98 mg. per 100 ml. for a 1-cm. path length, respectively; for methylglyoxal, 430 mμ and 1.05 mg. per 100 ml.; and for formaldehyde, 348 mμ and 1.14 mg. per 100 ml. The formaldehyde analysis was obtained from the same column by collecting the zone as it appeared in the filtrate during the development of the osazones.

Study of the Intermediates in Flame Combustion

The application of these chromatographic methods was first made to the combustion intermediates which were produced in a turbulent flame apparatus designed by Mr. Paul Oberdorfer of this laboratory. The carbonyl intermediates were isolated as the 2,4-dinitrophenylhydrazones, and the chromatographic procedures were applied to qualitative and quantitative studies of the intermediates. The quantitative work was extended to a study of the amounts of the three carbonyl compounds, glyoxal, methylglyoxal and formaldehyde, which were present in the flames of all the fuels studied.

Experimental

Materials.—All the gaseous hydrocarbons were obtained from the Matheson Company and were of a minimum of 99% purity. Ethane was the only exception; the purest grade available was a minimum of 95% purity. The liquid hydrocarbons were Phillips "Pure" grade, 99 mole per cent. minimum purity and were shown to have peroxide numbers of zero before use.

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(5) W. A. Schroeder, E. W. Malmberg, L. L. Fong, K. N. Trueblood, J. D. Landerl and E. Hoerger, *Ind. Eng. Chem.*, **41**, 2818 (1949); K. N. Trueblood and E. W. Malmberg, THIS JOURNAL, **72**, 4112 (1950). Merck reagent grade silicic acid purchased in the latter part of 1952 has proved to be unsatisfactory as a chromatographic adsorbent as received.

(6) O. L. Brady, *J. Chem. Soc.*, 756 (1931).

(7) W. A. Schroeder, P. E. Wilcox, K. N. Trueblood and A. O. Dekher, *Anal. Chem.*, **23**, 1740 (1951).

Turbulent Flame.—The turbulent flame was operated by injecting the vaporized fuel at high velocity into one end of an open Pyrex tube 4 ft. in length. A certain amount of air was aspirated by the action of the jet of fuel, and this combination served to produce a very turbulent flame at the inlet of the tube. Excess of fuel was always used so that the flame was in effect quenched by that excess.

Only a rough control could be made on the characteristics of the flame, but differences in the degree of turbulence could be judged approximately. The higher turbulence was obtained with greater relative amount and velocity of fuel injection. As shown below, the results with two series of oxidations with high and low turbulence correlate very well with each other and could be duplicated. The yield of dinitrophenylhydrazones was of the order of 0.05% on the basis of burned fuel; it was noticeably higher with flames of high turbulence.

Isolation of Carbonyl Intermediates.—A fraction of the outlet stream was drawn by suction through an absorbing train. The use of conventional dinitrophenylhydrazine reagent in 2 *N* hydrochloric acid was found to give complete absorption of the carbonyls even at high rates of gas flow when used with a sintered glass dispersion inlet for the gas.

Procedures for Confirmation of Identification.—The preliminary identification of the dinitrophenylhydrazone from chromatographic properties was confirmed by conventional methods as a standard procedure. In general, the proof was obtained readily by comparison of the X-ray diffraction pattern with that of an authentic sample. In some cases, for example the glyoxal osazone, difficulty was encountered in obtaining the known and unknown in the same polymorphic form. When glyoxal, methylglyoxal and formaldehyde appeared for every fuel which was studied, the confirmatory procedures were limited only to occasional checks. The identification was confirmed in all cases where the product included carbon–carbon and carbon–hydrogen bonds which were not present in the fuel of origin. In all cases there was complete agreement with the chromatographic properties.

Results

Results of Qualitative Analysis.—The results of a qualitative study of the carbonyl compounds which were isolated as dinitrophenylhydrazones from the turbulent flame oxidation are listed in Table I.

TABLE I

CARBONYL COMPOUNDS ISOLATED AS DINITROPHENYLHYDRAZONES FROM TURBULENT FLAME COMBUSTION

Methane: glyoxal, methylglyoxal, formaldehyde, acetaldehyde and acetone

Propane: glyoxal, methylglyoxal, formaldehyde, acetaldehyde, propionaldehyde, acetone, methyl ethyl ketone and possibly isobutyraldehyde

Benzene: glyoxal, methylglyoxal, formaldehyde and benzaldehyde

In each of these cases the preliminary chromatographic identification was confirmed by comparison of the X-ray diffraction pattern or in a few cases the infrared spectrum of the mull to the same measurements on authentic samples. Only in the case of methane was a complete analysis possible. Other zones were present in the chromatograms of the other oxidation products, but only in the case of methane and propane were intensive studies made of all components present. The results which are described in the next section show that glyoxal, methylglyoxal and formaldehyde were present in all the turbulent flame products. This result is particularly noteworthy in the cases of methane, benzene, cyclopropane, cyclopentane, cyclohexane and ethane.

Results of Quantitative Analysis.—The results of the analysis for the carbonyl intermediates which are common to all the fuels are presented in Table II. The fuels were chosen to give as wide a range of characteristics as possible. The critical compression ratio for these fuels[8] is given as a characterization of their behavior in an internal combustion engine. The critical compression is the compression ratio in a test engine at which a definite intensity of knock is reached.

TABLE II

RESULTS OF ANALYSIS FOR GLYOXAL, METHYLGLYOXAL AND FORMALDEHYDE IN THE CARBONYL FRACTION FROM TURBULENT FLAME COMBUSTION

Results are expressed in percentage of the component dinitrophenylhydrazone in the original precipitate

Component →	Glyoxal		Methylglyoxal		Formaldehyde		
Turbulence →	High	Low	High	Low	High	Low	CCR[a]
Fuel							
Normal paraffins							
Methane[b]	0.68		0.25		99		13.0
Ethane[c]	1.1	0.58	0.22	0.18	98	97	9.4
		.51		.20		98	
Propane	1.5	.99	0.41	.32	96	96	8.8
n-Butane	1.1	.72	.43	.22	89	98	5.3
n-Pentane	1.4	.85	.34	.34	78	84	3.2
n-Hexane	2.9	1.80	1.3	.76	79	60	3.0
n-Heptane	3.7	1.9	2.8	1.07	58	71	3.0
Branched-chain paraffins							
Isobutane	1.1	0.50	0.4	0.29	90	87	6.5
2,3-Dimethylbutane	0.92	.94	.29	.35	91	77	7.5
2,2,3-Trimethylbutane	1.0	.60	.5	.39	89	66	10.5
Cyclic compounds							
Cyclopentane	1.3	0.92	0.35	0.31	83	64	7.6
Methylcyclopentane	1.3		.41		75		5.5
Cyclohexane[c]	1.3	0.81	.29	0.25	82	50	4.7
	1.4		.22		81		
Cyclopropane	2.1		.61		64		6.7
Benzene	4.8	1.6	.59	0.33	59	56	15.0
Miscellaneous							
Ethylene	2.7		0.27		91		
Methanol	0.32		.10		95		
Ethanol	0.88		.10		79		

[a] CCR, critical compression ratio, 600 r.p.m. and 350° jacket temperature. [b] No carbonyl products could be obtained from methane at low turbulence. In other cases where only analysis at high turbulence is reported, only that combustion was run. [c] Second series of results is from the analysis of a duplicate oxidation run.

The analytical results in general are from single runs; when duplicate analyses were made, the mean deviation in the results for glyoxal and methylglyoxal was 0.01% or less and for formaldehyde 0.5%.

Discussion of Results

A number of the carbonyl intermediates which have been listed above may be regarded as degradative products of oxidation; as such they conform with the peroxide mechanism of oxidation of hydrocarbons. Other products, however, can result only from the formation of new carbon–carbon and carbon–hydrogen bonds in the flame, synthesis reactions. Methane will be chosen for discussion since the results are most clear-cut in that case. The most reasonable series of reactions by which acetaldehyde, acetone, glyoxal and methylglyoxal could be formed in the combustion of methane is

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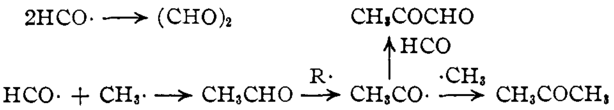
(8) W. G. Lovell, *Ind. Eng. Chem.*, **40**, 2388 (1948).



$$2HCO\cdot \longrightarrow (CHO)_2$$

$$HCO\cdot + CH_3\cdot \longrightarrow CH_3CHO \xrightarrow{R\cdot} CH_3CO\cdot \xrightarrow{\cdot CH_3} CH_3COCH_3$$

$$CH_3CO\cdot \xrightarrow{HCO} CH_3COCHO$$

With the appropriate modification for different fuels, this explanation can account for all the "synthesis products" which were isolated. The possibility that these products result from the formation and oxidation of higher hydrocarbon molecules has been eliminated. In the case of methane, relatively large amounts of ethane would have to be present in the products, but none was detected.

The necessity of including acyl radicals in the series of reactions is significant because the importance of acyl radicals in combustion has been in question.[9] Photochemical studies of carbonyl compounds[10] have shown that dimerization of formyl and other acyl radicals does occur at low temperatures, but the yield decreases and decomposition of the radicals becomes predominant at 125–150°. Evidence for greater stability of these radicals has been reported in recent photochemical work,[11] in thermal decomposition of dimethyl ether,[12] and in a methane flame.[12] In the flames studied in present investigations, temperatures of 500–800° were imposed for short periods of time; it appears therefore that with thermal excitation the stability of formyl and other acyl radicals is sufficiently great so that these groups may be important factors in high temperature oxidation.

The quantitative analyses for glyoxal, methylglyoxal and formaldehyde were performed to detect any correlation which might exist between the relative amounts of these products and the chemical structure and combustion characteristics of the fuels. From the results in Table II, no consistent difference is found in comparing fuels which are more or less susceptible to oxidation. This result is in accord with the present view that the difference between fuels of high and low critical compression ratio lies in the very early stages of the oxidation; these products, short chains and heavily oxygenated, are characteristic of the later stages of oxidation.

A number of correlations between chemical structure and the analytical results are apparent. In the normal paraffins, not until hexane and heptane are reached does the amount of glyoxal and methylglyoxal rise above a level which is essentially constant from ethane through pentane, a level which is just a little above that which is considered to be only recombination. When the occurrence of dimethylglyoxal is also considered, it would seem that in the C_6- and C_7-hydrocarbons a higher concentration of acetyl groups is encountered.

Highly branched hydrocarbons have a relatively high ratio of methylglyoxal to glyoxal when compared to the hydrocarbon with the same chain unsubstituted. In comparing cyclic and normal C_5- and C_6-paraffins the relatively close correspondence between open chain and ring compounds indicates the importance of the reaction of abstraction of hydrogen by terminal methylene groups. The large amounts of glyoxal and methylglyoxal from cyclopropane suggest that with this cycloparaffin with less reactive hydrogen the recombination of acyl radicals, occurs in preference to the reaction of abstraction of hydrogen to yield the aldehyde.

Acknowledgment.—The author is indebted to Miss Frances Zamnik for determination of infrared spectra of some of the dinitrophenylhydrazones. The interest of Professor C. E. Boord in this investigation is acknowledged with pleasure; this work is part of a fundamental study of the reaction of hydrocarbons directed by Professor Boord under sponsorship of U. S. Air Force Research and Development Command.

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[9] B. Lewis and G. von Elbe, "Combustion, Flames, and Explosions of Gases," Academic Press, Inc., New York, N. Y., 1951, Chapter IV.

[10] E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publ. Corp., New York, N. Y., 1946, Chapters V and VII.

[11] F. E. Blacet and J. G. Calvert, THIS JOURNAL, **73**, 66 (1951).

[12] G. C. Eltenton, *J. Chem. Phys.*, **15**, 455 (1947).