and the density data necessary for the calculation of parachors by the formula $P = \gamma^{1/4} [M/(D-d)]$, where M is molecular weight, γ is surface tension, D is the density of the liquid at the temperature of measurement of surface tension, and d is the density of the vapor at that temperature. Values of d are approximated from the empirical formula[4]

$$\log \frac{d_t}{d_f} = 5\left(\frac{T}{T_b} - 1\right)$$

in which d_t is the density of the vapor at the chosen temperature T, T_b is the boiling point absolute, and d_f is the density of the vapor at the boiling point. Approximate values of d_f are obtained from the formula $d_f = 0.0122 \times M/T_b$.

Of interest are the values for toluene, ethylbenzene, *n*-propylbenzene, isopropylbenzene and *n*-butylbenzene reported by Vogel.[5] Although a different method of measuring was used (cap. rise), only in case of isopropylbenzene is there a parachor variation as great as 0.1%. In this one case Vogel obtained a parachor 0.2% lower.

Although broader and more valid generalizations will be possible when values are available from additional and related compounds, there are certain constitutional variations that should be pointed out, particularly in the ortho, meta, para relationships. It was considered at one time that such position isomers showed no change. The meta isomer shows a parachor decrease of from 0.7 to 1.0% compared with the ortho. The para isomer shows a further decrease of from 0.1 to 0.15% in the parachor value. This latter decrease is admittedly of the order of magnitude of the experimental error. However the direction of the change is the same in three cases. The numerical values are shown in Table II.

Table II

Parachor Differences in Position Isomers

Compounds	Ortho to meta	% Change	Meta to para	% Change
Xylenes	1.80	0.6	0.24	0.1
1,2,3-Trimethylbenzene and 1,3,5-trimethylbenzene	2.15	0.7	..	..
Methylethylbenzenes	2.95	1.0	.47	0.15
Diethylbenzenes	3.37	0.9	.38	0.1

It may be noted in considering the series of normal monoalkyl compounds that the CH_2 increment from methyl- to ethylbenzene is abnormally low, 38.65. An abnormal low value for the CH_2 increment is also shown in comparing methyl- and ethyl-*p*-xylenes.[6]

Acknowledgment is made to the American Petroleum Institute, the National Bureau of Standards, and Dr. F. D. Rossini of the National Bureau of Standards for the samples and aid in securing the samples measured in this investigation. Acknowledgment is also made to the Office of Naval Research for financial support of this work.

Summary

1. The surface tensions and parachors of benzene and twenty homologs are reported at 20, 30 and 40°.

2. The variations in parachors of ortho, meta and para isomers are pointed out.

Emory University, Ga. Received June 1, 1949

[4] Sugden, Reed and Wilkins, *J. Chem. Soc.*, **127**, 1540 (1925).

[5] Vogel, *J. Chem. Soc.*, **40**, 3390 (1948).

[6] Unpublished data, this Laboratory.

[Contribution from the Chemical Laboratory of Northwestern University]

Oxygen Isotope Exchange in the Electric Discharge

By W. E. Roake[1] and Malcolm Dole*

Introduction

The problem of the enhanced O^{18} content of the atmosphere discovered by one of us in 1935[2] and more recently discussed by Kamen and Barker[3] has never been satisfactorily solved, either through a photosynthetic[4] or bacterial[5] explanation.

In this note we give for the first time what appears to be a possible explanation. We believe that the O^{18} enhancement takes place in the stratosphere under the influence of ultraviolet rays and by means of a random isotopic exchange between carbon dioxide and water. In order to give this idea a laboratory test, we decided to investigate the possibility of oxygen isotope exchange between carbon dioxide and oxygen and

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[1] Weston Fellow of the Electrochemical Society, 1945–1946; Charles A. Coffin Fellow of the General Electric Company, 1946–1947; present address: General Electric Company, Richland, Washington.

[2] M. Dole, This Journal, **57**, 2731 (1935); *J. Chem. Phys.*, **4**, 268 (1936); J. A. Swartout and M. Dole, This Journal, **61**, 2025 (1939).

[3] M. C. Kamen and H. A. Barker, *Proc. Nat. Acad. Sci.*, **31**, 8 (1945). This effect is called by Kamen and Barker, the "Dole Effect."

[4] C. H. Greene and R. J. Voskuyl, This Journal, **58**, 693 (1936); M. Dole and G. Jenks, *Science*, **100**, 409 (1944).

[5] M. Dole, R. C. Hawkings and H. A. Barker, This Journal, **69**, 226 (1947).

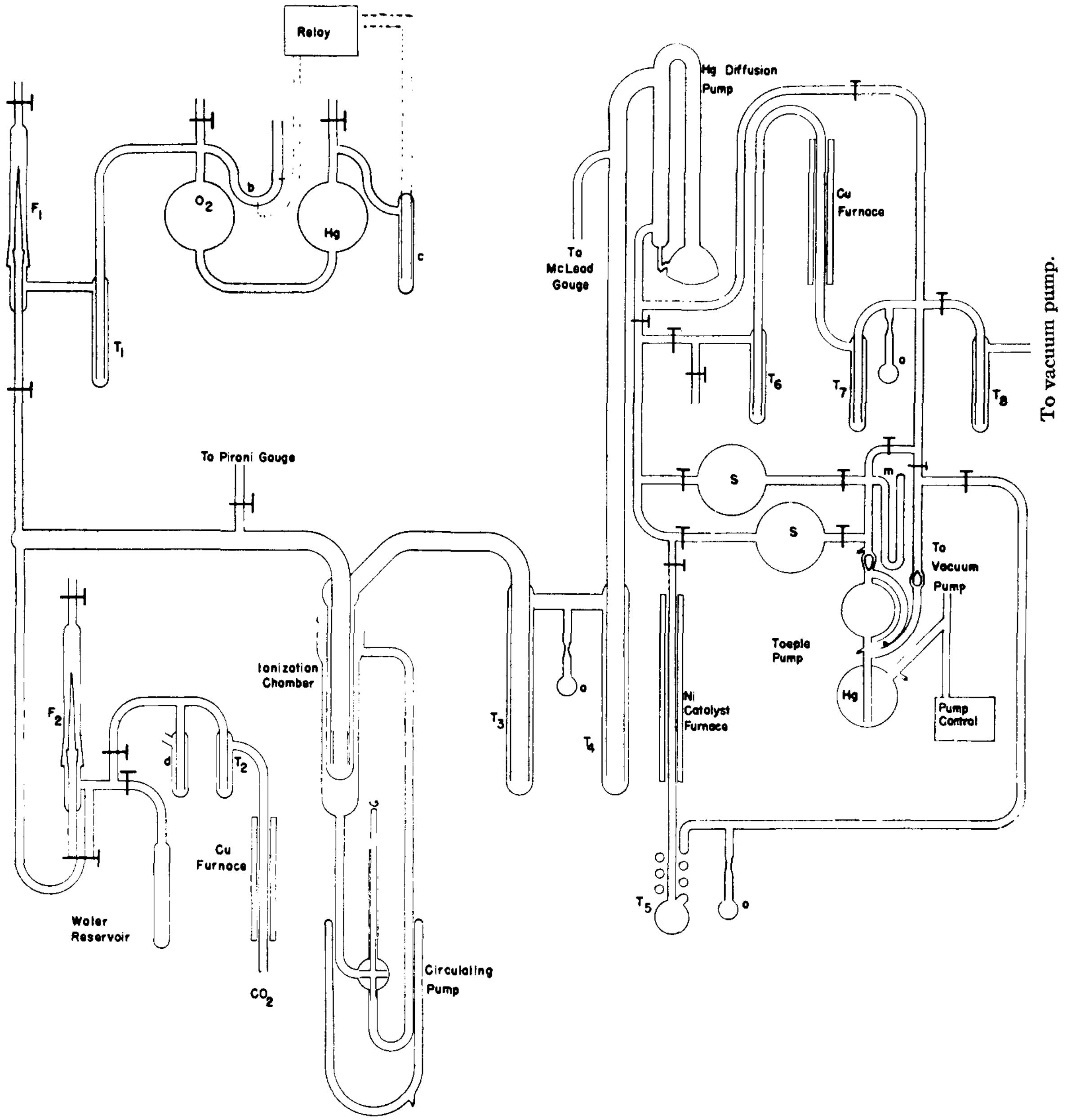

Fig. 1.

between water vapor and oxygen in the electric discharge at a temperature of −50°, the temperature of the isothermal portion of the stratosphere. As far as we know isotope exchanges in the electric discharge have never been studied.

The general plan of the research involved the mixing of oxygen and water vapor or oxygen and carbon dioxide gas at low pressures and passing them through a glow discharge cell at a continuous rate. After exposure to the action of the electric current, the gases were separated from each other and the oxygen isotope ratios measured. By comparison with the isotopic composition before exposure to the electric current, one could conclude whether isotopic exchange had occurred. We did not recirculate the gas until a steady state isotopic composition had been achieved, but this would be highly desirable to do.

Experimental

General Arrangement.—The general arrangement of the apparatus is shown in Fig. 1. In the upper left corner one can see the oxygen reservoir in which was placed ordinary tank oxygen or oxygen enriched in O^{18}. This oxygen was enriched to 1.95 times the normal O^{18} content, which is 950 parts per mil (thousand) or until the water made using this oxygen was 210 parts per million denser than Lake Michigan water.[6]

The flow of oxygen gas into the system was maintained at a constant rate by displacing it with mercury which in turn was displaced by mixed oxygen and hydrogen gases generated in the electrolysis cell, C, the rate of generation of these gases being controlled by the oxygen pressure. The reduction of the oxygen pressure to 1.4×10^{-2} mm. was accomplished through the capillary leak F_1. Water vapor or carbon dioxide at constant pressure flowed through the capillary leak F_2 at such a rate as to bring its pressure to about the same as that of the oxygen.

After passage through the ionization chamber which was cooled to about -40 or $-50°$ by means of alcohol which itself was cooled in a Dry Ice-trap and recirculated by means of an all glass pump, the mixed gases and reaction products were collected in various traps and reservoirs. The oxygen of the samples was then converted to water and the density measured.

The Ionization Chamber.—In order to produce as great ionization of the gases as possible as they flowed through the ionization chamber at the rate of about 100 ml. (S. T. P.) mixed gases per hour, the arrangement of electrodes in the discharge cell consisted of a grid anode supported midway between two plate cathodes and between the poles of a magnet so that the lines of magnetic force ran parallel to those of the electric field. This arrangement of electrodes and magnetic field is sometimes called the Philips Ionization Gauge.[7] The applied a.c. voltage was about 250 volts (R.M.S.), the magnetic field was about 1000 gauss (this is not critical), and the rectified direct current through the cell varied between 0.5 and 1 milliampere. Current at 1 milliampere running for forty hours (the time of electrolysis) is sufficient by Faraday's law to dissociate only about one per cent. or less of the gases present. However, the gas in the glow discharge will be dissociated to a far greater extent than this although the exact extent of dissociation is unknown. Under some conditions of the Penning-type discharge cell it is believed that practically all the gas that enters the glow region is ionized. It will be recalled that in this type of cell, the electrons oscillate rapidly back and forth through the grid when the grid is charged positively. In a quantitative study of the dissociation of water vapor in an ordinary electric discharge tube Linder[8] demonstrated that at a current of one milliamp., 5 molecules of water were dissociated per electron passed through the cell.

Recovery and Separation of Products.—In order to save space we shall describe in detail only our final two experiments in which deuterium-free hydrogen was used.

In the third experiment a crack developed in the Toepler pump, contaminating the system with atmospheric oxygen so that no data for the isotopic composition of the collected oxygen are given. In this experiment the recovery of hydrogen was 100%. The oxygen in the water used was enriched oxygen; the oxygen admitted to the ionization chamber was tank oxygen. No ozone or hydrogen peroxide could be detected in the traps.

The fourth experiment involved oxygen and carbon dioxide gas, the input oxygen being enriched and the carbon dioxide coming from a commercial tank. The output carbon dioxide and ozone were collected in a liquid-air-trap, T_3, while the output oxygen and carbon monoxide were recirculated through the copper furnace until all the oxygen had combined with the copper or had oxidized the carbon monoxide. The resultant carbon dioxide was collected in trap, T_5, and later reduced with deuterium-free hydrogen and the density of the water formed was measured. The copper oxide formed was also reduced with deuterium-free hydrogen to form another sample of water for analysis. The output carbon dioxide and ozone were separated by passage through a copper furnace where the ozone was collected as copper oxide. Reduction of the carbon dioxide and the copper oxide with deuterium-free hydrogen gave two more samples of water for analysis.

It has been shown by Chitani, Shigeo and Kanome[9] that no exchange of isotopes between carbon dioxide and copper oxide takes place at 300°, the temperature at which our copper furnaces were held.

Isotopic Analysis.—The submerged-float method of measuring the density of water served as the means for isotopic analysis. A tiny Pyrex float 0.1 cc. in volume was used. The small amount of water available for analysis was sometimes diluted quantitatively to increase its volume and was distilled in a vacuum purification line, first over hot copper oxide in a stream of oxygen, then from a crystal of chromic oxide and then from alkaline potassium permanganate and after a momentary boiling to free it from dissolved air, it was distilled *in vacuo* into the density observation tube. This treatment seemed to free most of our samples from dissolved impurities, but after a density measurement, the purification process was always repeated, in order to make sure that the water samples were as pure as this treatment would make them.

Temperature measurements were made with a platinum resistance thermometer in the bath out-

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(6) Professor Urey has suggested that the oxygen isotopic composition of different substances be expressed in parts per mil rather than in equivalent water density data. A difference in water density of one part per million because of variations in the O^{18} content is equivalent to 4.5 parts per mil on Urey's scale. Oxygen containing the twice normal O^{18} content would be 1000 parts per mil richer in O^{18}.

(7) See M. Dole, AECD-1867, declassified March 26, 1948, for a description of the behavior of the Philips Ionization Gauge; F. M. Penning, *Physica*, **4**, 71 (1937).

(8) E. G. Linder, *Phys. Rev.*, **38**, 679 (1931).

(9) T. Chitani, S. Shigeo and A Kanome, *Bull. Chem. Soc. Japan*, **17**, 228 (1942).

side the sample tube. The density measurements on any one sample were repeated until agreement to 0.1 part per million was obtained. It should be pointed out that because of complete distillation at every step, no fractionation of oxygen isotopes on distillation could occur.

Experimental Results and Discussion

The experimental results are indicated by the following equations in which the chemical symbols on the left side of the equation represent the substances entering the ionization chamber while the right-hand symbols represent the substances after passing through the ionization chamber. The superscripts indicate the difference in the density in parts per million of water made from the element concerned and normal hydrogen or oxygen as the case may be and Lake Michigan water. The density of deuterium-free water has been taken to be −16.0 p. p. million, and the density of water containing normal hydrogen and air oxygen, +6.0 p. p. million in the following representation of the results.

Expt. 3:

$$O^{7.9} + H_2^{-16.0}O^{226.6} \longrightarrow O^{?} + H_2 + H_2^{-16.0}O^{236.1}$$

Expt. 4:

$$CO_2^{+6.5} + O_2^{156} \longrightarrow O_2^{134} + CO + CO^{17.3} + O_3^{65}$$

$$CO + O_2^{134} \longrightarrow CO_2^{90} \text{ (This reaction in copper furnace)}$$

In order to find out whether any exchange of oxygen isotopes had taken place, some water containing oxygen enriched in O^{18} and deuterium-free hydrogen was used in Expt. 3. In this experiment the oxygen of the water definitely appears to have become further enriched in O^{18} despite the fact that we expected its density to become less, as it would have if an isotopic exchange equilibrium had been established or if any isotopic exchange even of a random nature had taken place. Apparently under the conditions of our experiment no oxygen isotope exchange between water vapor and gaseous oxygen occurred. This fact is not too surprising in view of the observations of a number of investigators that water does not dissociate into hydrogen and oxygen atoms in the electric discharge, but into hydrogen atoms and OH radicals.[10]

Turning now to Expt. 4 in which carbon dioxide was used, we see definite evidence for oxygen exchange, the oxygen has become slightly depleted in O^{18} and the carbon dioxide slightly richer while the ozone and carbon monoxide, both molecules formed in the electric discharge, also showed evidence of exchange of the O^{18} isotope. This experiment seems to prove definitely the possibility of oxygen isotope exchange between oxygen and carbon dioxide in the electric discharge.

Conclusions

Returning now to the problem of the enhanced O^{18} content of the atmosphere, the results given above would seem to indicate the greater possibility of enhancement due to exchange between carbon dioxide and oxygen rather than to exchange between water vapor and oxygen. Our results, of course, do not preclude the possibility of a slow exchange of oxygen isotopes between oxygen and water vapor, because of the rapidity with which the gases flowed through our discharge cell. Nevertheless under comparable conditions exchange between carbon dioxide and oxygen takes place more rapidly than between water vapor and oxygen.

Because the O^{18} isotope at equilibrium concentrates in carbon dioxide when carbon dioxide and water are brought in to equilibrium to the extent of 8 to 10 p. p. million in equivalent water density, the enhanced O^{18} content of the atmosphere can be understood on the basis of a random (*not* at equilibrium) exchange of O^{18} isotope between oxygen and carbon dioxide. In other words the atmosphere could easily pick up its excess O^{18} from either a random exchange between oxygen and carbon dioxide or an exchange at equilibrium (*not* a random exchange) between oxygen and water vapor. The results of this investigation indicate that the oxygen–carbon dioxide exchange is the more likely of the two.[11]

At this time we cannot say anything about the rate of this exchange and the rate of circulation of oxygen, water vapor and carbon dioxide between the troposphere and the upper regions of the stratosphere and ionosphere. It would be interesting to study the isotopic composition of oxygen from different geographical locations and from different altitudes in order to discover whether any vertical circulation exists or not. Near the level of the oceans and in the tropics we should expect the oxygen to have a composition nearer to that of the oxygen liberated in the photosynthesis reaction than to the oxygen of the stratosphere. Such a difference could amount to as much as 4 or 5 p. p. million in water density.

Acknowledgment.—We are indebted to the Alexander Dallas Bache Fund of the National Academy of Sciences for funds for the purchase of the platinum resistance thermometer and auxiliary equipment and to the Penrose Fund of the American Philosophical Society for a grant which defrayed the cost of the magnet construction.

Summary

No evidence for the exchange of oxygen isotopes between oxygen and water vapor could be discovered on passing the two through an electric discharge cell at low pressures and at −40° in the presence of a parallel magnetic field. However, a significant exchange was found to exist when oxygen and carbon dioxide were the gases

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[10] O. Oldenberg, *J. Chem. Phys.*, **3**, 266 (1935); W. H. Rodebush, C. R. Keizer, F. S. McKee and J. V. Quagliano, THIS JOURNAL, **69**, 538 (1947).

[11] For a more detailed discussion see M. Dole, *Science*, **109**, 77 (1949).

in the cell. The relation of these results to the problem of the enhanced O^{18} content of the atmosphere is discussed, and a theory for the latter is given which seems for the first time to be quantitatively possible.

EVANSTON, ILL. RECEIVED APRIL 26, 1949

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Heats of Adsorption and Molecular Configuration. The Pentanes on Carbon Black

BY R. A. BEEBE,[1] G. L. KINGTON,[1] M. H. POLLEY[1] AND W. R. SMITH[2]*

In an investigation of the factors which contribute to the energy of binding between physically adsorbed molecules and a solid surface, it is obviously necessary to consider the nature of the adsorbate molecules as well as the state of the solid surface. Earlier work[3] which has been reported from these Laboratories has shown that the heats of physical adsorption for a specific gas such as nitrogen or butane may vary considerably on different carbon surfaces such as Spheron 6 and Graphon carbon blacks.

If we limit our consideration to a single solid surface, we still find instances of marked differences in the binding energies, as shown by differences in the heats of physical adsorption, for different adsorbates on the same adsorbing surface. These differences may be due to such obvious factors as difference in molecular weight as illustrated by the heats of adsorption of *n*-butane and *n*-pentane on carbon black,[3] or to difference in polarizability of the adsorbate molecules as in the comparison of the heats of adsorption of *n*-butane and 1-butene on silica gel.[4] However, in certain instances, these differences in binding energy appear to arise from less obvious causes. For instance it has been found that the heat of adsorption for nitrogen exceeds that for oxygen on a relatively bare anatase surface[5] by about 1 kcal. per mole of adsorbate although molecular weight considerations would lead one to predict the reverse relationship in the heat values.

In the present investigation, we have chosen to work with the two isomeric C_5 hydrocarbons: *n*-pentane and neopentane (2,2-dimethylpropane), on the same carbon black surface at 0°. In these two hydrocarbons we have adsorbates with identical molecular weights and closely similar chemical properties, but with different geometric configurations. Although cyclopentane is not a true isomer of the other two pentanes studied, it has been included in the present work. Our experimental results show that there are marked differences in the energies of binding of these C_5 hydrocarbons to the carbon black surface, which can be plausibly explained on the basis of molecular configuration.

Experimental

Materials.—The carbon black adsorbent was a sample of a commercial black designated as Spheron 6. The properties of this pigment, which have been extensively studied, have been described in detail in previous publications.[3] Further studies on carbon black structure have been made more recently by Hall with dark-field illumination in the electron microscope.[6]

The *n*-butane and neopentane were Phillips research grade; the *n*-pentane and cyclopentane were Phillips pure grade. All these hydrocarbons were of warranted purity 99 mole per cent. or better. Any air which might have been introduced during transfer was removed by evacuating the system while the hydrocarbon was frozen out in a side trap at −195°. This operation was followed by several bulb to bulb distillations with evacuation between distillations.

Apparatus.—The apparatus used in this work has been previously described.[3] In order to be as certain as possible about the value for the heat capacity of the calorimeter we have made altogether seventeen heat calibration determinations. The probable error of the mean for these calibrations was 0.37%.

Results and Discussion

Altogether, ten successful heat runs were carried out at 0° on two samples from the same batch of Spheron 6 carbon black. It was possible to determine the adsorption isotherms simultaneously with the calorimetric measurements. The results of these experiments are shown in Figs. 1 and 2.[7] B. E. T. plots of the isotherm data yielded straight lines up to 0.25 relative pressure in all cases. From these plots it was possible to determine the values of V_m and of c of the B. E. T. equation which are given in Table I.

TABLE I

Adsorbate	V_m, cc./g.	c	σ, sq. Å./molecule
n-Butane	9.2	40	45
n-Pentane	8.0	58	53
Neopentane	7.3	53	57
Cyclopentane	8.8	23	47

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* Harvard University Ph.D. 1935.

(1) Amherst College, Amherst, Mass.

(2) Godfrey L. Cabot, Inc., Boston, Mass.

(3) (a) Beebe, Biscoe, Smith and Wendell, THIS JOURNAL, **69**, 95 (1947); (b) Beebe, Polley, Smith and Wendell, *ibid.*, **69**, 2294 (1947).

(4) Beebe and Smith, *Ind. Eng. Chem.*, **41**, 1431 (1949).

(5) Kington, Polley, Smith and Beebe, forthcoming publication.

(6) Hall, *J. Applied Phys.*, **19**, 271 (1948).

(7) (a) The values of E_L, the heats of liquefaction of the hydrocarbons under investigation, are indicated at the right of Fig. 2; (b) the order of the experiments was as follows: Run 82, *n*-butane; Run 83, *n*-pentane; Run 84, neopentane; Run 85, neopentane; Run 86, cyclopentane; Run 87, *n*-butane; Run 97, *n*-butane; Run 98, *n*-butane; Run 99, *n*-pentane; Run 100, cyclopentane. Sample 1 of the carbon black was used in Runs 82–87; Sample 2, in Runs 97–100.