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SUBJECT:
ONDERWERP: THE NITRIC ACID OXIDATION OF COAL. PART IV.
APPLICATION OF THE GRAPHICAL-STATISTICAL METHOD TO THE INTERPRETATION OF THE INVESTIGATIONS ON THE NITROHUMIC ACIDS.

DIVISION:
AFDELING: CHEMISTRY.

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OPSOMMING.

'n Nuwe grafies-statistiese metode om reaksiemeganismes en -produkte voor te stel, en wat deur Van Krevelen ontwikkel is, is gebruik in die verklaring van die reaksies van die nitrohumiensure verkry uit die oksidasie van steenkool.

FUEL RESEARCH INSTITUTE OF SOUTH AFRICA.

THE NITRIC ACID OXIDATION OF COAL. PART IV.

APPLICATION OF THE GRAPHICAL-STATISTICAL METHOD TO THE INTERPRETATION OF THE INVESTIGATIONS ON THE NITROHUMIC ACIDS.

SUMMARY:

A new graphical statistical method of representation of reaction mechanisms and products, developed by Van Krevelen[1], has been used in the interpretation of the reactions of the nitrohumic acids from coal oxidation.

In a recent publication Van Krevelen[1] developed a new graphical-statistical method for the study of problems connected with the structure and reaction processes of coal. In this method use is made of a diagram in which the hydrogen-carbon atomic ratio is plotted against the oxygen-carbon ratio. He showed that reactions such as oxidation, dehydrogenation, hydrogenation, dehydration, demethanation and decarboxylation are represented by straight lines. He proved mathematically that in the diagram decarboxylation is represented by a straight line which connects the composition of the starting material (C/H, C/O ratios) with the point C/H = 0, C/O = 2. Similarly dehydration is represented by straight lines which have a slope equal to 2. Oxidation and deoxygenation are indicated by horizontal straight lines, while hydrogenation and dehydrogenation are represented by vertical straight lines.

This method has now been applied to the products from various reactions on the mixture of ether-insoluble nitrohumic acids obtained from the nitric acid oxidation of coal as was described in Part II[2] of this series, as well as to the products from fraction I, which was prepared by a method of fractional precipitation of an

acetone solution/.....

acetone solution of the mixture with ether. The method has been found to be extremely useful in indicating the nature of the reactions.

A. REACTIONS:

The method was applied to the results of the investigations on the mixture of acids as well as to those on fraction I, since the results of the former are related to those of the latter.

(i) Reactions on the humic acid mixture:

Various reactions on the ether-insoluble mixture of nitro-humic acids were described in Part II[2] and are again given briefly below. The H/C and O/C ratios of the reaction products were calculated and plotted on a H/C : O/C diagram shown in Figure 1. The reactions, the percentage composition of the products, the atomic ratios and the number of the product are summarised in Table I.

(a) Alkali-treatment:

The ether-insoluble product obtained directly from the oxidation was found to be only partially soluble in acetone and alcohol. However, if the product was dissolved in alkali and the alkaline solution acidified immediately, a product was obtained which was completely soluble in both solvents but still insoluble in ether. In Part II[2] it was suggested that this change was most probably due to the hydrolysis of anhydrides and/or lactones. From the slope of the line joining 1 (original product) to 2 (alkali-treated product) in Figure 1 it may be deduced that alkali-treatment involves a hydration reaction.

(b) Prolonged treatment of the alkali-treated ether insoluble mixture with concentrated nitric acid yielded ether-insoluble products of almost constant composition (Table I, No.3). From Figure 1 it is clear that this reaction involves the opposite of (a) i.e. a dehydration reaction.

(c) and (d)/............

(c) and (d) The mixture of alkali-treated ether-insoluble acids on reduction with zinc dust and hydrochloric acid yielded a product which was separated chromatographically into two fractions. (Table 1, numbers 4 and 5). From Figure 1 it may be deduced that the hydrogenation is accompanied by deoxygenation.

(e) Decarboxylation:

The alkali-treated ether-insoluble product was decarboxylated in a heated suspension of copper powder in quinoline. Product 7, Table I, was obtained and it was found that carbon dioxide was evolved during the reaction. The reaction (e), Figure 1, which represents this reaction appears to be most interesting. The direction of the line is not what one would normally expect from a loss of carbon dioxide only. It appears that in the decarboxylation both carbon dioxide and water are eliminated as was already deduced from a study of the analytical results as such (see Part II loc. cit.).

(f) Oxidation of the reduced product:

Reaction (f) Figure 1 which represents the nitric acid oxidation of the reduced product, indicates that the oxidation is accompanied by a dehydrogenation reaction.

TABLE I

ATOMIC RATIOS OF REACTION PRODUCTS OF THE NITROHUMIC ACID MIXTURE

Origin of product	Percentages C	H	N	Atomic ratios H/C	O/C	Number
Ether-insoluble product direct from oxidation	50.76	2.48	3.78	0.58	0.63	1
Ether-insoluble product after alkali-treatment	45.79	3.24	3.80	0.85	0.78	2
Alkali-treated product treated with nitric acid for 27 hours and subsequently treated with alkali.	51.41	2.36	4.77	0.55	0.60	3

Zinc-hydrochloric/.......

TABLE I (CONT.)

ATOMIC RATIOS OF REACTION PRODUCTS OF THE NITROHUMIC ACID MIXTURE

Origin of product	Percentages			Atomic ratios		Number
	C	H	N	H/C	O/C	
Zinc-hydrochloric acid reduction product of alkali-treated mixture Separated chromatographically. Fraction I	60.82	4.89	2.82	0.96	0.38	4
do Fraction II	54.67	5.73	1.38	1.26	0.52	5
HNO_3-oxidation product of 4.	51.19	3.09	4.09	0.72	0.61	6
Decarboxylation product of alkali-treated product.	65.95	3.44	7.50	0.63	0.26	7

(ii) Reactions of nitrohumic acid fraction I:

Nitrohumic acid fraction I was obtained from the mixture of the ether-insoluble acids by precipitation of an acetone solution of the mixture with ether (Part III). Various reactions were carried out on this fraction and the H/C and O/C ratios of the products are plotted on the diagram in Figure 2.

(a) Decarboxylation:

The nitrohumic acid fraction I (1, Table II) was decarboxylated with copper powder in the presence of quinoline and phenol. A fraction of the product was found to be soluble in methyl ethyl ketone (2, Table II) while the residue (3, Table II) was found to be insoluble in this solvent.

The decarboxylation reaction is represented in Figure 2 by lines a and a^1. The reaction by which product 2 is formed approaches a pure decarboxylation reaction. The reaction product is soluble in organic solvents such as methyl ethyl ketone. The reaction by which product 3 is formed (reaction line a') appears to involve both decarboxylation and dehydration and is similar to that obtained from

the mixture/.........

the mixture of humic acids (see Figure 1). This product is insoluble in most organic solvents but is soluble in pyridine. It was stated in Part II that the decarboxylation reaction on the mixture of nitrohumic acids appears to be accompanied by a condensation reaction in which water is lost. This view is further substantiated by the fact that in the presence of phenol, this condensation reaction appears to be at least partially, inhibited.

To clarify the above deductions it may be mentioned that an empirical formula of $C_{60}H_{40}N_4O_{38}$ was calculated for fraction I^2. For the simultaneous loss of water and carbon dioxide e.g. 5 molecules of each, a product represented by (H/C = 0.55, O/C = 0.42) in Figure 2 is obtained.

Fraction I was reduced with titanous chloride and hydrochloric acid to give product 4 of Table II. As in the case of the mixture of acids the hydrogenation is accompanied by deoxygenation which would be normally expected from the reduction of nitro groups, etc.

(c) <u>High-pressure hydrogenation:</u>

Fraction I was subjected to high-pressure hydrogenation in the presence of Raney-nickel catalyst. Three products were obtained viz. a product soluble in methyl ethyl ketone, a product insoluble in methyl ethyl ketone and a viscous oil. These products are presented as 5, 6 and 7 in Table II and in Figure 2.

Like the titanous chloride reduction the high pressure hydrogenation appears to consist of both hydrogenation and deoxygenation. The titanous chloride reduction product, 4, and the high-pressure hydrogenation products, 5 and 6, fall on one line, appearing to indicate progressive hydrogenation and

deoxygenation/.........

deoxygenation by one type of reaction. The liquid product 7, appears to be a product of hydrogenation of product 6.

TABLE II

ATOMIC RATIOS OF REACTION PRODUCTS OF NITROHUMIC ACID FRACTION I

Origin of product	Percentages C	H	N	Atomic Ratios H/C	O/C	Number
Nitrohumic acid fraction I	50.86	2.99	4.13	0.70	0.61	1
Decarboxylation product I	63.13	4.47	2.66	0.85	0.35	2
Decarboxylation product II (Methyl ethyl ketone-insoluble)	67.54	3.52	4.21	0.62	0.26	3
Titanous chloride reduction product.	57.35	4.08	1.23	0.85	0.48	4
High-pressure hydrogenation product (Methyl ethyl ketone-soluble)	62.38	5.16	2.42	0.91	0.43	5
High-pressure hydrogenation product (Methyl ethyl ketone-insoluble)	58.92	4.48	2.96	0.99	0.36	6
High-pressure hydrogenation product (liquid)	61.15	7.77	1.00	1.51	0.36	7

REMARKS:

Van Krevelen applied the graphical-statistical method for the determination of the structure and the reaction processes of coal. He illustrated this method for reactions of acetone and benzoic acid. It is found, for example, that the line joining the points representing benzaldehyde (Figure 2, 8, H/C = 0.86, O/C = 0.14) and benzoic acid (Figure 2, 9, H/C = 0.86, O/C = 0.29) has the direction of the lines representing oxidation. The line joining benzyl alcohol (Figure 2,10, H/C = 1.14, O/C = 0.14) to benzoic acid, however, does not correspond with any of the lines representing the different reactions. If it is therefore known that the product (benzyl alcohol) has been oxidised and one assumes that oxidation has actually taken place to yield the oxidised product (benzoic acid), it may be deduced that the oxidation process has been accompanied by a dehydrogenation process viz. benzylalcohol to benzaldehyde (see dotted line between points 8 and 10).

The conclusions drawn from Figures 1 and 2 in connection with the reaction processes of humic acids have been based on the way of reasoning explained above. When, however, the H/C and O/C ratios of a number of related products are plotted on a diagram, without knowing the types of reactions that are involved in their production, it is practically impossible to deduce what relation the one bears to the others since any number of different reaction lines may be followed from one point to another.

REFERENCES.

[1] van Krevelen, D.W., Fuel, 1950, 29, 269.
[2] van Duuren, B.L., J.S.A. Chem. Inst., New Series, 4, 25.

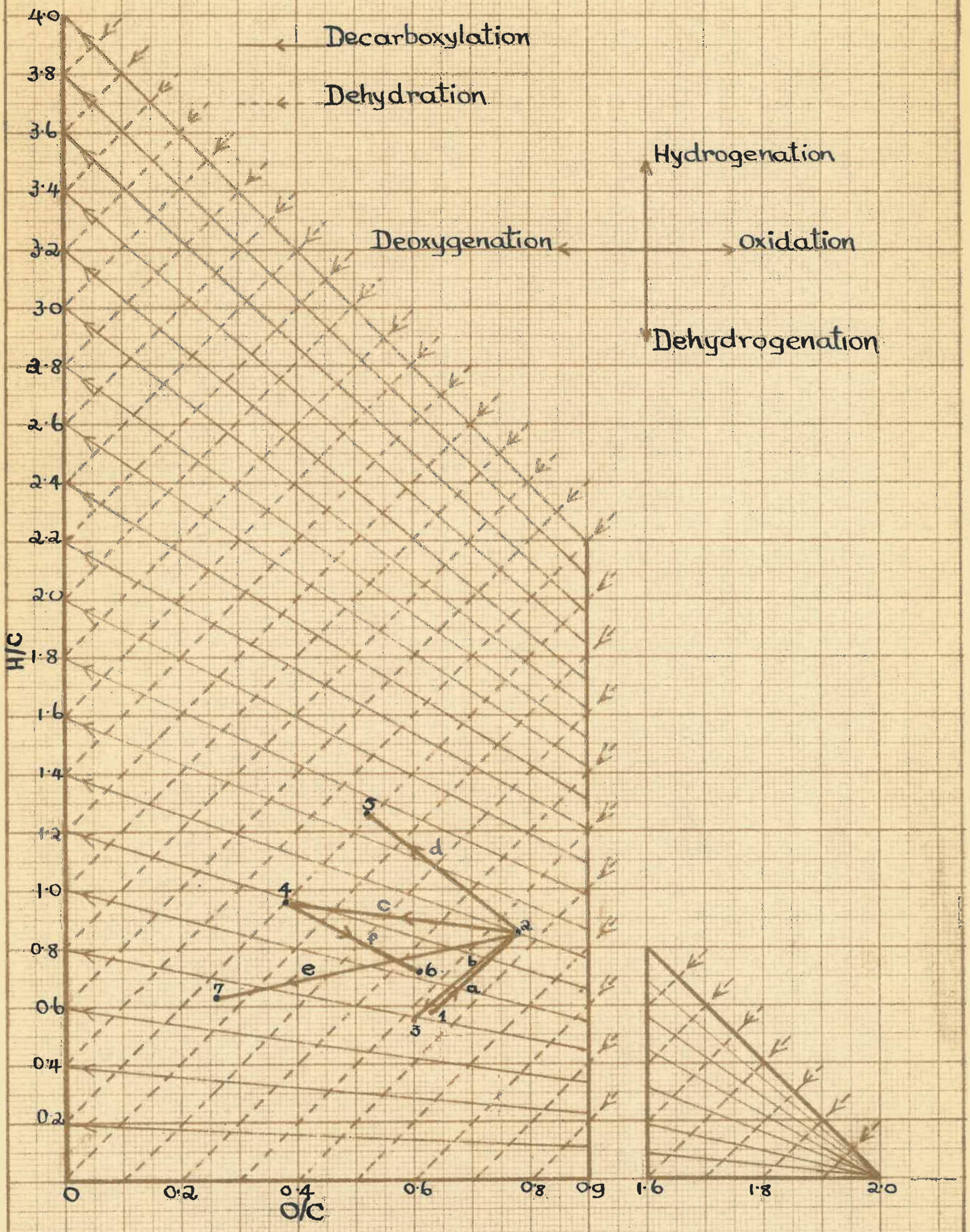

FIG. 1 : REACTIONS OF THE NITROHUMIC ACID MIXTURE

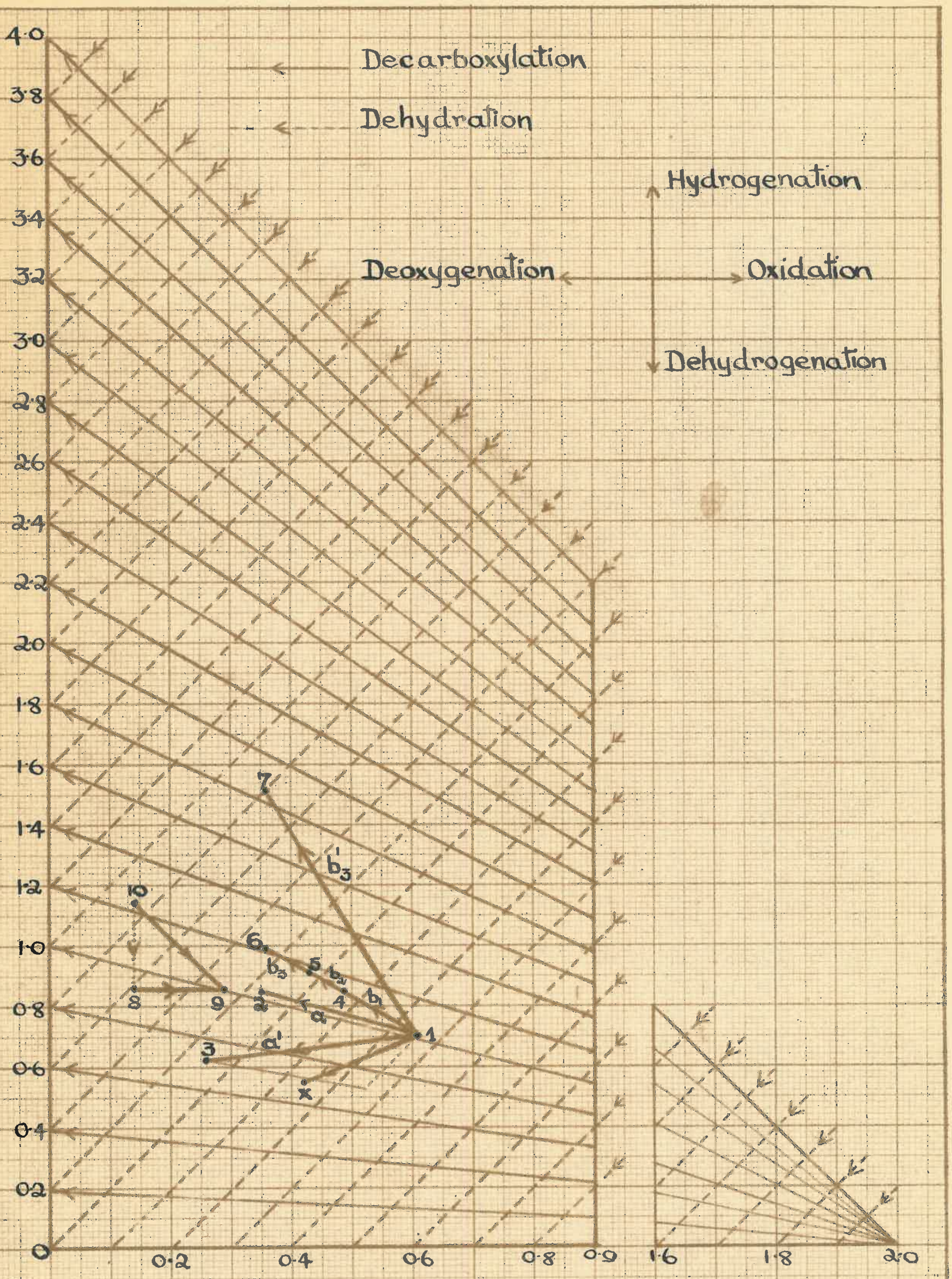

FIG. 2 : REACTIONS OF NITROHUMIC ACID FRACTION 1