

GASEOUS

DECOMPOSITION PRODUCTS OF RANCID OILS

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THE phenomenon of gaseous evolution, which may be observed on heating a rancid or oxidized oil, hitherto has escaped notice in the literature relative to rancidity and its mechanism. This seeming neglect of this phase of the problem may be attributed to the general supposition that such "gas-sing" is due to expulsion of dissolved air and offers no very promising field for investigation.

Hilditch and Sleightholme,¹ in oxygen absorption experiments, found that when they attempted to carry the oxidation to extreme limits "water vapor and probably carbon dioxide and volatile organic compounds were evolved in sufficient amounts to cause a sharp break, or even a cessation, in the oxygen absorption." . . . "If the heated oil was submitted to reduced pressure vigorous effervescence and frothing occurred and, in the later stages of oxidation, this behavior took place to some extent even in the cold."

About ten years ago, Dr. Frank C. Vibrans and the writer were engaged in a study of factors affecting the development of rancidity in the laboratories of The Procter & Gamble Company. Having ascertained the rate of peroxide formation under various conditions an attempt was made to determine its rate of decomposition. For this purpose, sealed glass tubes of oxidized oil of high peroxide content were heated at 100° C. for periods varying from a few days to several weeks in duration. At the end of one week the last trace of peroxide had disappeared, as measured by our test which depended upon the oxidation of ferrous to ferric iron. Nevertheless the oils were found to be extremely rancid.

On opening the tubes all were found to be under considerable pressure and bubbles of gas were observed rising through the oil. A few micro tests showed traces of CO₂ and established the presence of an inflammable gas which burned with a slightly luminous flame.

Experiments were then conducted

on a larger scale arranged so that sufficient gas could be collected for analysis. Some results are shown in Table I. The most surprising features of these analyses is the

in the composition of this gas from that obtained from the earlier experiments except that the higher oxygen content may be indicative of a slight accidental air leakage. The

TABLE I

No.	Kind of Oil and Temperature	cc. Oil Used	cc. Gas Collected	Analysis of Gas Collected (Per Cent by Volume)						
				CO ₂	O ₂	CO	C ₂ H ₄	H ₂	C ₂ H _{2n+2}	N ₂
1	Rancid Cottonseed Oil, 100° C.	510	70.1	0.6	0.1	2.6	0.0	64.9	1.0	30.8
2	Another portion of above, 100°-200° C.	533	66.7	4.0	0.6	9.7	0.0	44.2	2.0	39.5
3	Very Rancid Compound, 100° C.	533	85.7	0.6	0.4	4.2	0.4	77.3	0.6	16.5
4	Another portion of above, 100°-200° C.	533	92.7	10.0	0.0	11.2	0.2	70.7	1.0	6.9
5	Sample No. 4 on further heating, 200°-230° C.	533	48.7	31.2	0.4	20.1	0.7	41.5	4.0	2.1

presence of a large proportion of hydrogen in every sample of gas collected. All gas analyses were performed according to standard methods: CO₂, O₂, CO and unsaturated hydrocarbons were absorbed by appropriate solutions; H₂ was selectively oxidized in a CuO tube at 300° C.; saturated hydrocarbons were burned in a slow combustion pipette and the residual nitrogen was determined by difference. A striking increase is noticeable in the amounts of CO₂ and CO in those samples of gas collected by thermal decomposition at higher temperatures.

Quite recently a careful check experiment was conducted as follows:

Four hundred ninety grams of refined and filtered cottonseed oil, which had been allowed to become rancid by exposure to oxidation at room temperature for about fifteen months, were placed in a flask so arranged that the evolved gases would be collected over mineral oil by displacement from an inverted burette. The flask was heated on a steam bath in such a manner that the temperature of the oil itself was about 85° C. Gas evolution began in about four to six hours and continued for over a week. Most of the gas was collected during the first three days. Table II shows the data obtained from this experiment.

The gas analyses were performed with great care with mercury as the confining liquid. It will be noted that there is no essential difference

nitrogen found in all samples is obviously the inert residue from dissolved air.

The evolution of hydrogen from a rancid oil seems paradoxical indeed. Rancidity is itself a result of oxidation and it is difficult to reconcile these two apparently contradictory phenomena. No explanation

TABLE II

Total gas collected = 156.6 cc. (0° C. and 760 mm.).			
% CO ₂ = 0.71		% O ₂ = 3.34	
% CO = 2.63		% C ₂ H ₄ = 0.0	
% H ₂ = 66.73		% C ₂ H _{2n+2} = 0.35	
% N ₂ (by diff.) = 26.24			
Oil Characteristics			
Peroxide No. 2	=	226.5	0.3
Iodine No. (Wijs)	=	105.4	102.1
Acid No.	=	0.4	2.6
Saponification No.	=	191.5	195.6
Carbonyl No. 3	=	17.2	5.6
Hydroxyl No. 4	=	29.6	18.9
N _D (48° C.)	=	1.4638	1.4638

or even tentative mechanism for this unexpected reaction is here attempted or proposed. For the benefit of any who may care to theorize, it may be helpful to point out the following relationships:

1. A drop in peroxide number from 226.5 to 0.3, according to the notation here used, indicates a disappearance of 226.2 millimols of peroxide per kilogram of oil.

2. A drop in hydroxyl number from 29.6 to 18.9 is equivalent to disappearance of 190.7 millimols —OH/kg. oil.

3. A drop in carbonyl number from 17.2 to 5.6 is equivalent to

disappearance of 206.8 millimols. $C=O/kg.$ oil.

4. 104.5 cc. H_2 (at $0^\circ C.$ and 760 mm.) from 490 grams of oil is equivalent to 9.52 millimols $H_2/kg.$ oil.

5. 226.5 peroxide number, if completely reduced by HI in the iodine number determination, would cause the iodine number of the oil before heating to be too low by 5.7. Hence the true iodine number, corrected for this peroxide effect, of the oil before heating should have been $105.4 + 5.7 = 111.1$. The true drop in iodine number would then be $111.1 - 102.1 = 9.0$ and this

drop is equivalent to 354.5 millimols I_2 per kg. oil. It is probable that the evolved hydrogen is at first in the atomic state and as such is highly reactive toward double bonds. From these considerations it is quite likely that the hydrogen collected represents only a small fraction of the total formed during decomposition of the peroxides. The lowering in iodine number is entirely adequate to account for thirty-five to forty times as much hydrogen as was actually collected.

It is hoped that the data here presented may stimulate further thought and experimentation toward

increasing our knowledge of the mechanism of oil rancidity. The writer wishes to express his appreciation to Dr. F. C. Vibrans of the Institute of American Meat Packers for his assistance and cooperation during the early experiments and to The Procter & Gamble Company for permission to publish.

References

¹J. S. C. I. Vol. 51, No. 6, pp. 39T-44T (1932).

²D. H. Wheeler, Oil and Soap 9, pp. 89-97 (1932).

³Stillman and Reed, Perfumery & Essential Oil Record 33, pp. 278-86 (1932).

⁴Andrews and Reed, Oil and Soap 9, pp. 215-18 (1932).

REPORT OF JOURNAL COMMITTEE 1934

IN OUR report last year, we told you something about the financial difficulties we were having in securing advertising. This year I am glad to be able to report that our Journal is on a much sounder financial basis than formerly and is no longer showing red figures. This is, of course, due to our success in securing new advertising and retaining most of our old advertisers.

There is one point, however, to which I wish to call the attention of our members. Most of us are prone not to mention the fact that our attention was called to certain equipment, chemicals, etc., which we purchase through the advertising appearing in OIL & SOAP. This is one simple way of letting our advertisers know the value of using OIL & SOAP as an advertising medium.

I am listing below a list of the advertisers in our Journal during the past year and wish again to urge you to use this list in purchasing your equipment and supplies:

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In reviewing the editorial content of the Journals, I find that during the past year we have published 43 original scientific papers and 24 committee reports. In addition, our Journal has carried, each month, two full pages of abstracts which are of great interest to our members; also, there were the write-ups of our meetings, etc., and other matters of general interest.

We think the quality of the papers being produced in our Journal is getting better each year. Our

Journal is, and should be, one means of increasing the membership in our Society. As the advertising increases, we will also be able to increase the editorial content.

During the year, the untimely death of Dr. David Wesson created a vacancy on the Editorial Advisory Board. By a unanimous vote of the Journal Committee, Dr. William E. Anderson of Yale University was appointed to fill the vacancy. The terms of Dr. A. D. Holmes, Dr. G. S. Jamieson, and Mr. H. P. Trevithick expire this year. The Journal Committee has unanimously asked them to accept appointment on the Board for the next three years and they have accepted.

The latter part of this year we have been able to convince our publishers of the wisdom of printing our editorial matter so that it may be bound without the inclusion of any advertising matter, and also all of our scientific papers will appear continuously in future issues.

In conclusion, the Journal Committee solicits your criticisms and suggestions for the improvement of the Journal.

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