FRI 21/1951

Form No. F.R.I. 47.

REPORT No. 21

OF 1951

RAPPORT No. 21

VAN 1951

U1D413

FUEL RESEARCH INSTITUTE

OF SOUTH AFRICA.

BRANDSTOF-NAVORSINGS-INSTITUUT

VAN SUID-AFRIKA.

SUBJECT:
ONDERWERP: A NOTE ON THE CONDENSATION REACTIONS OF METHYL ETHYL KETONE.

DIVISION:
AFDELING: CHEMISTRY.

NAME OF OFFICER:
NAAM VAN AMPTENAAR: B. L. VAN DUUREN.

W.P.—69328—17/1/50

FUEL RESEARCH INSTITUTE OF SOUTH AFRICA.

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A NOTE ON THE CONDENSATION REACTIONS OF METHYL ETHYL KETONE.

By: B.L. van Duuren.

During an investigation of the nitric acid oxidation product of coal a neutral liquid was isolated. Subsequent experiments proved that this liquid did not constitute a part of the oxidation product proper. Its most likely source was considered to be the methyl ethyl ketone which had been used as solvent in the extractions. The oxidation product was extracted from acid and from alkaline solutions at various stages with methyl ethyl ketone, and it was therefore not unlikely that the latter could have undergone condensation reactions during extractions as well as during removal of the solvent from the various extracts.

The neutral liquid was separated chromatographically on alumina into a number of fractions. These fractions were purified by vacuum distillation and analysed. From the ultimate analyses the following formulae were calculated for 4 of these fractions.

TABLE 1.

MOLECULAR FORMULAE OF NEUTRAL LIQUIDS.

Boiling Point.	Empirical Formula.	Molecular Weight (Found)	Possible Molecular Formula.
75°C/1 mm.	C_4H_8O	123	$C_8H_{16}O_2$
92° - 94°C/ 17.5 cm.	C_3H_6O	130	$C_6H_{12}O_2$
68° - 70°C/ 0.15 mm.	$C_7H_{11}O_2$	162	$C_7H_{11}O_2$
64° - 65°C/ 0.11 mm.	$C_7H_{11}O_2$	159	$C_7H_{11}O_2$

The following information regarding condensation products of methyl ethyl ketone were found in the literature. Concentrated

alkali/.....

alkali gives, on standing with methyl ethyl ketone in the cold, a water-insoluble, ether-soluble liquid of boiling point 187° - 192°C at atmospheric pressure. This liquid gave on analysis the formula $C_8H_{16}O_2$. Franke and Köhler (1) suggested the following formula for this substance:

$$CH_3 \cdot CH_2 \cdot \underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}(OH) \cdot CH_2 \cdot CO \cdot CH_2 \cdot CH_3$$

3 methyl heptanol - (3) - one - (5).

The same authors (loc. cit.) found that methyl ethyl ketone on treatment with concentrated alkali at elevated temperature or with sodium ethoxide or alcoholic caustic potash yielded an unsaturated ketone $C_8H_{14}O$, for which they suggested the formula:

$$CH_3 \cdot CH_2 \cdot C(CH_3) = CH \cdot CO \cdot CH_2 \cdot CH_3$$

This substance belongs to the class of homomesitones or homomesityl oxides discussed by Porlizza and Gatti [2].

Of the compounds isolated from the coal oxidation products after extractions involving the use of methyl ethyl ketone, only the one of empirical formula C_4H_8O seems to be a known substance. Although the substance has not been finally identified it is most likely the ketone alcohol described by Franke and Köhler (1). The others do not conform in analyses with any of the known condensation products of methyl ethyl ketone.

These findings merit further investigation of the problem and also indicate that caution should be exersized in the use of methyl ethyl ketone as solvent in extractions.

EXPERIMENTAL:-

The mixture of neutral liquids were separated into two fractions with light petroleum and the two fractions separated further by chromatography on alumina. The various fractions were purified by vacuum distillation and analyses:

Liquid 1:/.....

Liquid 1: (Bp. 75°C/1.0 mm.) Analysis 1:-

4.189 mg. gave 10.395 mg. CO_2 and 4.270 mg. H_2O.

0.495 mg. + 5.655 mg. camphor gave depr. 27.5°.

Found:- C, 67.72; H, 11.40%; Mol. Wt., 123.

$C_8H_{16}O_2$ requires:- C, 66.66; H, 11.11%; Mol. Wt., 144.

Liquid 2: (Bp. 92° - 94°C/17.5 cm.) Analysis 2:-

4.223 mg. gave 9.790 mg. CO_2 and 4.030 mg. H_2O.
0.875 mg. + 8.295 mg. camphor gave depr. 31.4°.

Found:- C, 63.28; H, 10.68%; Mol. Wt., 130.

$C_6H_{12}O_2$ requires:- C, 62.07; H, 10.34%; Mol.Wt., 116.

Liquid 3: (Bp. 68° - 70°/0.15 mm.) Analysis 3:-

4.500 mg. gave 10.940 mg. CO_2 and 3.535 mg. H_2O.
0.598 mg. + 6.313 mg. camphor gave depr. 22.6°.
Found:- C, 66.39; H, 8.79%; Mol. Wt., 162.
$C_7H_{11}O_2$ requires:- C, 66.14; H, 8.66%; Mol.Wt., 127.

Liquid 4: (Bp. 64° - 65°C/0.11 mm.) Analysis 4:-

4.460 mg. gave 10.820 mg. CO_2 and 3.440 mg. H_2O.
0.780 mg. + 7.692 mg. camphor gave depr. 24.7°.
Found:- C, 66.16; H, 8.63%; Mol. Wt. 159.
$C_7H_{11}O_2$ requires:- C, 66.14; H, 8.66%; Mol. Wt. 127.

REFERENCES.

1. A. Franke & T. Köhler, Ann., 433, 314 (1923).

2. M. Porlizza & O. Gatti, Gazetta, 25, 224 (1925).
