SOME AIR OXIDATION PRODUCTS OF DI-2-ETHYLHEXYL SEBACATE

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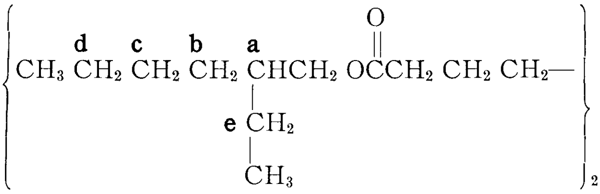
Synthetic lubricants based on diesters are used widely in extreme-temperature military applications (Cohen et al., 1953). The identification of the gaseous oxidation products of such compounds is of interest, in view of a biochemical toxicity attributed to these vapors (Treon et al., 1954). Autocatalytic oxidation (Murphy and Ravner, 1956) and pyrolysis rate (Sommers and Crowell, 1955) studies have been carried out on di-2-ethylhexyl sebacate, a typical such base stock. The former report gave peroxide, acid, carbon dioxide, and water analyses while the latter determined only acid content.

In general, the decomposition of this ester might be expected to follow one of two oxidation paths. In the liquid phase at 50 to 150° C, preferential attack (Walsh, 1946) at the tertiary carbon, **a,** via the usual alkyl hydroperoxide intermediate, should yield mostly ethyl butyl ketone.



$$\left\{ CH_3\,\overset{\mathbf{d}}{CH_2}\,\overset{\mathbf{c}}{CH_2}\,\overset{\mathbf{b}}{CH_2}\,\overset{\mathbf{a}}{\underset{\substack{|\\ \mathbf{e}\ CH_2\\ |\\ CH_3}}{CH}}CH_2\,O\overset{\overset{O}{\|}}{C}CH_2\,CH_2\,CH_2— \right\}_2$$

In the vapor phase above 200° C, additional attacks (Malmberg et al., 1955) at the various methylene sites will become increasingly important. The anticipated volatile monofunctional carbonyl compounds in the five carbon (C_5) and lower range should be acetaldehyde, **d** and **e**, propionalydehyde, **c**, and butyraldehyde, **b**. A $C_2{:}C_3{:}C_4 = 2{:}1{:}1$ degradation proportion would be predicted upon this basis.

EXPERIMENTAL PROCEDURE

A di-2-ethylhexyl sebacate sample (10.000 g) in an all-glass apparatus was heated by means of an electrical controlled salt bath. The contents were continuously air aspirated and the exit vapors were passed into a scrubber containing 2,4-dinitrophenylhydrazone solution. The induction period, defined as the time necessary for cloudiness to appear in the scrubber, and the rate of formation of carbonyl compounds were observed over various temperatures (table 1).

DISCUSSION

The precipitates were collected and were chromatographed (Malmberg, 1954) to determine the nature and relative quantity of the different carbonyl compounds. Each individual 2,4-dinitrophenylhydrazone band assignment was confirmed both by chromatography of known mixtures and by infrared comparison spectra of the eluted derivatives. A zone due to ethyl butyl ketone was present in the two lowest temperature runs, but the quantity produced decreased as the temperature rose. Acetaldehyde, propionaldehyde, and butyraldehyde were found as the predominent products in the last two runs and were present to the proportion of 2:1:1. Acrolein or crotonal derivatives were not observed upon the column.

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These results tend to indicate that the ester decomposes by a predominent liquid-phase oxidation route in the temperature range where it is ordinarily used as a lubricant. However, as the temperature rises, the increasing vapor pressure of the ester leads to larger amounts of small carbon oxidation products.

TABLE 1

Oxidation of di-2-ethylhexyl sebacate as measured by the rate of hydrazone formation

Temperature in °C	Induction period in hr	Total time in hr	Total ppt in mg	Rate in mg/hr
160	2.50	13.0	325	25
190	1.00	6.5	292	45
210	0.42	4.0	266	67
297	0.17	0.9	168	193
333	0.08	0.8	535	640

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