electric moment and θ the angle between d_0 and the dipole axis. It would be difficult, in view of the changes in orientation of the dipole along the chain to derive at present any closer basis of relation other than analogy between the two formulations. It is interesting to note, however, that the value for the slope constant S in equation (2) is practically identical for the three halogen acids. The electric moments of the C–halogen bond for the three halogens are likewise very nearly equal. The relative magnitude of the slope constants, however, bears no obvious relation to that of the electric moments of the substituents.

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The Mechanism of the Diene Synthesis

BY EDWIN R. LITTMANN

The observation of Diels and Alder[1] that a yellow color appears during the synthesis of the colorless α-phellandrene-maleic anhydride suggests that the reaction mechanism involves a colored intermediate compound. Such a mechanism would imply a second order followed by a first order process, and in the absence of side reactions the observed reaction rate constants should approach those for a first order reaction as the concentration increases.

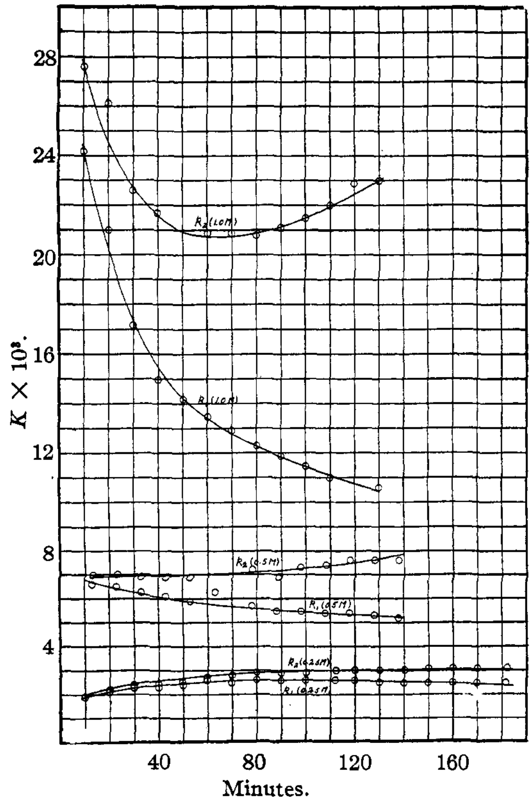

Fig. 1.—Reaction rate constants of α-phellandrene–maleic anhydride.

To test this matter measurements of the rate of reaction between α-phellandrene and maleic anhydride in acetone solutions have now been carried out at 0.25, 0.50 and 1.0 molality.

The α-phellandrene (Schimmel and Company) had the following properties: specific rotation (sodium light), −110.7°; refractive index (white light), 1.4775, and density, both at 20°, 0.856. The maleic anhydride (Eastman Kodak Company) was completely soluble in benzene and was used without further purification. The solutions, cooled to 25°, after thoroughly mixing were transferred to 2-dm. polarimeter tubes and observations of the rotation taken at definite intervals. The temperature of the polarimeter tube was maintained at 25 ± 0.5° by means of an air jet directed on the tube.

The results obtained are given in Fig. 1 in which the rate constants were calculated from the integrated forms of the standard rate equations. The values of the computed constants indicate that the reaction is more nearly unimolecular in the dilute than in the concentrated solutions and therefore it appears either that some other reaction mechanism is involved or that side reactions take place.

In order if possible to isolate the hypothetical polymer formed in the reaction, 6.8 g. of α-phellandrene and 4.9 g. of maleic anhydride were mixed without the use of any solvent and heated to 55–65° whereupon a violent reaction ensued which subsided in a few minutes. After standing for fifteen minutes the mixture was distilled at 3–5 mm. from an oil-bath at 250° until no more distillate was formed. The non-volatile residue was extracted repeatedly with ether, but only a small portion dissolved. The residual white powder when washed with methanol and dried gave, on analysis, 68.7% carbon and 7.27% hydrogen. Its molecular weight by the Rast method was found to be approximately 1220. These data agree with an empirical formula approximating either $C_{46}H_{56}O_{12}$ or $C_{60}H_{74}O_{15}$, giving 69.0 or 69.6% carbon, 7.00 or 7.17% hydrogen, and a molecular weight of 800 or 1034, respectively.

Since α-phellandrene and maleic anhydride were the only substances present, and since the

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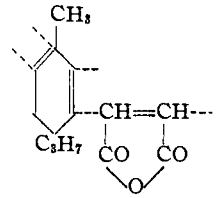
[1] *Diels and Alder, Ann.*, **460**, 98 (1927).

analysis precluded either terpene or maleic anhydride polymers, it seemed highly probable that a polymeric addition product had been obtained in which the average ratio of maleic anhydride to terpene was 4:3 or 5:4. Polymers of probable similar type have been reported by Wagner-Jauregg.[2]

The size of the polymeric α-phellandrene-maleic anhydride molecule and probable excess of anhydride over terpene would seem to exclude any but linear type polymers and would indicate a bifunctional character of the intermediate. An intermediate of the type



would satisfy the requirements of both polyfunctionality and color and would explain the formation of a polymeric material of the type $C_4H_2O_3$ $(C_{10}H_{16}-C_4H_2O_3-)$ $C_4H_2O_3$ in which there is an alternation of terpene and maleic anhydride molecules.

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WILMINGTON, DELAWARE
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[2] Wagner-Jauregg, *Ber.*, **63**, 3213 (1930).

COMMUNICATION TO THE EDITOR

THE DECOMPOSITION OF GASEOUS PARAFFINS INDUCED BY ETHYLENE OXIDE

Sir:

Heckert and Mack [THIS JOURNAL, **51**, 2706 (1929)] obtained evidence that *n*-butane and *n*-pentane were "cracked" in presence of decomposing ethylene oxide at temperatures (—400°) at which the normal rate of decomposition of these paraffins is negligible. We have confirmed this observation in the case of *n*-butane, and have in addition shown that isobutane and propane, but not ethane, also undergo appreciable decomposition under like conditions.

Our method consisted in analyzing the gases, pumped from the reaction vessel, for carbon monoxide (acid Cu_2Cl_2) and for total olefins (bromine water). At a total pressure of about 500 mm. and a temperature of 425°, the following results were obtained.

HC.	Initial ratio HC./C_2H_4O	Ratio C_nH_{2n}/CO by anal.
C_2H_6	1.6	<0.05
C_3H_8	1.6	.55
i-C_4H_{10}	1.7	.75
n-C_4H_{10}	1.6	1.2
n-C_4H_{10}	4.1	4.5
n-C_4H_{10}	8.0	12.

It will be noted that the relative amount of olefin increases with the complexity of the paraffin; and also (in the case of *n*-butane at least) with the relative amount of paraffin initially present. Since the C_nH_{2n}/CO ratio can exceed unity, it is evident that reaction chains may be set off in the paraffin.

The rate of pressure increase falls off rapidly as reaction proceeds, which may indicate that the products of the paraffin decomposition are inhibiting reaction. A similar result is obtained in the uninduced decomposition of paraffins [*e. g.*, Pease and Durgan, *ibid.*, **52**, 1262 (1930)].

The effect of temperature on the C_nH_{2n}:CO ratio is not great.

The accelerated decomposition of acetaldehyde in presence of ethylene oxide noted by Fletcher [*ibid.*, **58**, 534 (1936)] has been confirmed.

This work is being continued.

PRINCETON UNIVERSITY L. S. ECHOLS, JR.
PRINCETON, N. J. R. N. PEASE
RECEIVED JUNE 24, 1936