

**REACTION IN ETHYLENE-HYDROGEN MIXTURES
INDUCED BY OXYGEN**

Sir:

It has been found that small amounts of oxygen in ethylene-hydrogen mixtures cause greatly increased *initial* reaction rates in the homogeneous reaction at 538°. Reaction was carried out at constant volume. Pressure drops during the first, second and third minutes (ΔP_1 , ΔP_2 , ΔP_3) appear in the accompanying table.

TABLE I

REACTION IN ETHYLENE-HYDROGEN MIXTURES INDUCED
BY OXYGEN

| Run | H ₂ | Initial press., mm. C ₂ H ₄ | N ₂ | O ₂ | ΔP_1 mm./min. | ΔP_2 mm./min. | ΔP_3 mm./min. |
|-----|----------------|--|----------------|----------------|--------------------------|--------------------------|--------------------------|
| 1 | 576 | 192 | ... | ... | 4.5 | 4 | 4.5 |
| 2 | 572 | 191 | ... | 5.8 | 63 | 10 | 4.5 |
| 3 | 191 | 573 | ... | 5.8 | 29 | 6 | 4.5 |
| 4 | ... | 770 | ... | 5.8 | 18 | 6 | 4.5 |
| 5 | ... | 382 | 382 | 5.8 | 5 | 3 | 2.5 |

The initial acceleration is much greater in hydrogen-rich mixtures (*cf.* No. 2 with No. 3 and No. 4). The effect could be due to accelerated ethylene polymerization, known to be induced by oxygen [Lenher, THIS JOURNAL, 53, 3752 (1931)]. It seems more likely that the hydrogenation reaction itself is affected.

Further experiments are in progress.

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**THE CALCULATION OF MOLAR POLARIZATION
OF SOLUTES AT INFINITE DILUTION WITH
HEDESTRAND'S FORMULA**

Sir:

It has been suggested by Svirbely, Ablard and Warner [THIS JOURNAL, 57, 652 (1935)] that Hedestrands method of extrapolation should not be considered of general application if the values of α and β of the equation

$$P_{\infty} = A \left(M_2 - \beta \frac{M_1}{\rho_1} \right) + B\alpha \quad (1)$$

are not constant for varying concentration or in other words if the dielectric constant and density are not linear functions of the concentration.

In the derivation of the above equation Hedestrands [Z. physik. Chem., B2, 428 (1929)] says that for small concentrations the dielectric con-

stant (ϵ) and the density (ρ) of the solutions are given by the equations

$$\epsilon = \epsilon_1 + \alpha N_2 \quad \rho = \rho_1 + \beta N_2 \quad (2)$$

and then proceeds to substitute these in the equation for the polarization of the solute. Then in the limit, $N_2 = 0$, we have $P_2 = P_{\infty}$, $\epsilon = \epsilon_1$, $\rho = \rho_1$, and $N_1 = 1$. The values of α and β are consequently $(d\epsilon/dN_2)_{N_2=0}$ and $(d\rho/dN_2)_{N_2=0}$, which may be seen from equation (2). Now if the dielectric constant and density of the solution are linear functions of the concentration, α and β are the slopes of these straight lines. If α and β are functions of the concentration then they are the slopes of the tangents to the dielectric constant and density curves at zero concentration.

As it is rather difficult to obtain a tangent to a curve it was suggested by Hedestrands (*loc. cit.*) that α and β obtained from equation (2) be plotted against the concentration and extrapolated to infinite dilution.

This was carried out for the compounds of Svirbely, Ablard and Warner and the results are listed below.

| Compound | Svirbely, Ablard, Warner | | Recalculated | |
|-----------------|--------------------------|----------------------|--------------|----------------------|
| | P_{∞} | $\mu \times 10^{18}$ | P_{∞} | $\mu \times 10^{18}$ |
| d-Pinene | 192 | 2.67 | 184 | 2.60 |
| d-Limonene | 95 | 1.56 | 96 | 1.57 |
| Methyl benzoate | 170 | 2.52 | 172 | 2.54 |
| Ethyl benzoate | 166 | 2.43 | 159 | 2.34 |

These are good checks and should serve to indicate that Hedestrands formula can be used for substances in which the dielectric constant and density are not linear functions of the concentration.

It is interesting to note that compounds like the phenylacetylenes [Otto and Wenzke, THIS JOURNAL, 56, 1314 (1934)] and the phenylethylenes [Otto and Wenzke, *ibid.*, 57, 294 (1935)] have constant α and β while the dialkoxyalkanes [Otto, *ibid.*, 57, 693 (1935)] have slowly increasing value of α . The values of α for the compounds of Svirbely, Ablard and Warner increase very rapidly and it might be as they suggest indication of varying degrees of dipole orientation such as has been shown to exist in solutions of alcohols.

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