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

	Initial press., mm.				ΔP_1	ΔP_2 mm./min.	ΔP_3
Run	H_2	C_2H_4	N_2	O_2			
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 Hedestrand's method of extrapolation should not be considered of general application if the values of α and β of the equation

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

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 Hedestrand [*Z. physik. Chem.*, **B2,** 428 (1929)] says that for small concentrations the dielectric constant (ϵ) and the density (ρ) of the solutions are given by the equations

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

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 $(\mathrm{d}\epsilon/\mathrm{d}N_2)_{N_2 = 0}$ and $(\mathrm{d}\rho/\mathrm{d}N_2)_{N_2 = 0}$, 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 Hedestrand (*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.

	Svirbely, Ablard, Warner		Recalculated	
Compound	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 Hedestrand's 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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