COMMUNICATIONS TO THE EDITOR

INHIBITION OF THE HYDROGENATION OF ETHYLENE BY NITRIC OXIDE

Sir:

Since the dissociation of ethane to yield ethylene and hydrogen is inhibited by nitric oxide,[1] one might expect the reverse reaction to be similarly affected. We find this to be the case. Times to 16% ethylene converted (by analysis) are given in the following table for mixtures of 180 mm. ethylene and 540 mm. hydrogen with and without 20 mm. nitric oxide.

Temp., °C.	t_{16} (min.) Pure	NO added	Ratio
500	38	48	0.79
550	6.2	13.5	0.46

The effect of the nitric oxide tends to fade out after about 20% reaction, just as in the case of the dissociation of *n*-butane.[2] The above ratios are therefore not a true measure of the maximum inhibition. There is little doubt, however, that the nitric oxide is more effective at the higher temperature.

Stavely[1] found that with 150 mm. of ethane at 620° the initial rates of pressure increase with and without addition of 20 mm. of nitric oxide were in the ratio 0.086. Although the dependability of pressure measurements is open to serious question, it is nevertheless evident that this result is in qualitative agreement with our data for the reverse reaction. A rough extrapolation of the latter gives 0.22 for the ratio at 620°. The maximum inhibition (at zero time) would be less than this.

We believe this is the first case in which forward and reverse reactions have been shown to be equally subject to inhibition.

(1) Stavely, *Proc. Roy. Soc.* (London), **162A**, 557 (1937).
(2) Echols and Pease, THIS JOURNAL, **61**, 1024 (1939).

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INHIBITION OF ETHYLENE POLYMERIZATION BY NITRIC OXIDE

Sir:

A number of investigators have shown that the polymerization of ethylene is subject to acceleration by substances believed to give rise to radicals.[1] We find that the reaction is also subject to inhibition by nitric oxide. Thus, with 720 mm. of ethylene at 500° the time to 20% reaction is twenty-four minutes. Addition of 20 mm. of nitric oxide increases this to seventy-three minutes, the ratio of times being 0.33.

As in the hydrogenation of ethylene and the dissociation of *n*-butane,[2] the effect of nitric oxide fades out as reaction proceeds. The maximum effect is therefore greater than the data given above would indicate.

Since the polymerization of ethylene is subject to inhibition as well as acceleration, there can be little doubt that the reaction is of the radical chain type.

(1) Metal alkyls: H. S. Taylor and Jones, THIS JOURNAL, **52**, 1111 (1930); azomethane: O. K. Rice and Sickman, *ibid.*, **57**, 1384 (1935); oxygen: Lenher, *ibid.*, **53**, 3737, 3752 (1931).
(2) See previous communication, and Echols and Pease, THIS JOURNAL, **61**, 1024 (1939).

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SODIUM SALT OF 2-METHYL-1,4-NAPHTHOHYDROQUINONE DIPHOSPHORIC ACID ESTER

Sir:

Fieser and Fry [THIS JOURNAL **62**, 228 (1940)] have described some sulfuric and phosphoric acid esters of substituted 1,4-naphthohydroquinones. In this Laboratory we have been occupied for some time with similar phosphoric acid esters and have also prepared such materials as were described by the above workers. In our syntheses we also isolated the intermediate phosphoryl chlorides and free phosphoric esters.

In particular we have investigated the pharmacology of the sodium salt of 2-methyl-1,4-naphthohydroquinone diphosphoric acid ester, and have found that by a slightly modified Ansbacher vitamin K eighteen-hour bioassay technique [*J. Nutrition*, **17**, 303 (1939)] the above material in doses of 0.6 to 0.8 gamma per chick administered subcutaneously reduces the clotting time to below ten minutes. Intravenously, the activity is similar, while the dose for oral effectiveness lies below 2 gamma, the minimum dose not yet having been determined. The lethal dose in mice by both