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.)		Ratio
	Pure	NO added	
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 subcutaneous and intravenous administration is approximately 450 mg./kg. More complete pharmacological investigations will be reported elsewhere. All preliminary tests indicate an enormous margin of safety and absence of serious side reactions in any but the highest doses.

When it is considered that the anhydrous sodium salt has the molecular weight of 422 as compared with the molecular weight of 172 for 2-methyl-1,4-naphthoquinone, the most active material (0.5 gamma) hitherto reported, it appears that this sodium salt represents probably the most active antihemorrhagic substance known when compared on a molecular basis with methylnaphthoquinone. It also encourages speculation as to whether the antihemorrhagic effects of 2-methyl-1,4-naphthoquinone, of its reduced form, and of like substances, are not mediated through a phosphoric ester.

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THE PHOTOCHEMICAL REACTIONS OF OXALYL CHLORIDE AND PHOSGENE WITH CYCLOHEXANE

Sir:

The occurrence of the hypothetical —COCl free radical has been postulated as an intermediate in certain photochemical reactions: notably in the formation of phosgene [Bodenstein, *et al.*, *Z. physik. Chem.*, **B3,** 459 (1929)] and in the photochemical decompositions of both phosgene and oxalyl chloride [Rollefson, *et al.*, THIS JOURNAL, **56,** 1089 (1934); **58,** 443 (1936)]. In line with the program under way in this Laboratory on chain reactions in solution involving atoms and free radicals, we have studied the photolysis of both phosgene and oxalyl chloride dissolved in cyclohexane. In both cases we have been able to isolate the acid chloride of cyclohexane carboxylic acid. The yields appear to be quantitative. The over-all reactions are

$$C_6H_{12} + (COCl)_2 \longrightarrow C_6H_{11}COCl + HCl + CO$$
$$C_6H_{12} + COCl_2 \longrightarrow C_6H_{11}COCl + HCl$$

The following experiment with oxalyl chloride is typical of the procedure used. A 100-cc. flask (Pyrex glass) containing 25.2 g. of cyclohexane (0.3 m.) and 9.6 g. of oxalyl chloride (0.075 m.) was illuminated by a 300-watt tungsten lamp placed immediately below the flask. The heat from the lamp kept the reaction mixture refluxing gently. Gases were evolved. These were collected after passing through a trap at −80° and shown to consist of equal parts of carbon monoxide and hydrogen chloride. After twenty-four hours, the reaction mixture was fractionated and it was found that 4.2 g. of oxalyl chloride had reacted to form 4.1 g. of the acid chloride of cyclohexanecarboxylic acid (b. p. 99–101° at 52 mm.). The calculated yield is 4.8 g. The identification of the product was made by a determination of the neutralization equivalent and the preparation of the amide, m. p. 185–186°.

Phosgene reacts with cyclohexane in a similar manner. In this case quartz apparatus was used (a quartz reaction flask with a quartz mercury arc). In both cases the reaction takes place in the liquid phase as shown by identical results obtained in experiments in which care was taken to shield the vapor phase.

There can be little doubt that the reaction of phosgene and oxalyl chloride with cyclohexane in the light takes place through a free radical or atom mechanism in which the formation of the —COCl free radical plays a conspicuous rôle. In the gas phase the primary process in the photolysis of oxalyl chloride and phosgene has been postulated as follows

$$\text{(1)} \quad COCl_2 \xrightarrow{h\nu} \text{—}COCl + Cl^-$$
$$\text{(2)} \quad (COCl_2) \xrightarrow{h\nu} \text{—}COCOCl + Cl^-$$
$$\text{(or 2)} \quad (COCl)_2 \xrightarrow{h\nu} 2\,\text{—}COCl$$

In solution the absorption of light appears to be accompanied by the same primary step. This must be followed by reaction of the photolytic fragments with the hydrocarbon solvent. We hope to elaborate on the mechanism in our next publication.

The method of direct carboxylation appears to be fairly general and has been applied to a number of saturated hydrocarbons and their halogen derivatives. We are now engaged in studying the carboxylation of other types of organic compounds and the effect of various catalysts. It is of importance that means other than light of inducing the reaction have been found (*i. e.*, small quantities of organic peroxides are quite effective).

We are actively engaged in working out the details of this investigation and we hope to publish a full report shortly.

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