

from that of monohydric phenols. Replacement of both hydroxy groups by methoxy groups, however, markedly reduces the reactivity (see graph).

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Jan. 21.

¹ Nozaki, K., and Bartlett, P. D., *J. Amer. Chem. Soc.*, **68**, 1686 (1946).

² Swain, C. G., Stockmayer, W. H., and Clarke, J. T., *J. Amer. Chem. Soc.*, **72**, 5426 (1950).

³ Bartlett, P. D., and Nozaki, K., *J. Amer. Chem. Soc.*, **69**, 2299 (1947).
Tipper, C. F. H., *J. Chem. Soc.*, 2966 (1952).

⁴ Cosgrove, S. L., and Waters, W. A., *J. Chem. Soc.*, 388 (1951).

Reaction of Nitric Oxide with Gaseous Hydrocarbon Free Radicals

THE inhibiting effect of nitric oxide upon radical chain-reactions in the decomposition of certain organic compounds is well known¹, and such mechanisms as



have been invoked to explain this inhibition. Although Küchler and Theile² obtained traces of cyanide from the nitric oxide-inhibited decomposition of ethane, in no case has the nitroso compound been isolated in such reactions. Coe and Doumani³ prepared nitroso-methane from the photolysis of *tert.*-butyl nitrite.

As part of a systematic study of decomposition-rates of metal alkyls, we have pyrolysed mercury di-*isopropyl* in a flow system using a carrier gas of nitrogen and nitric oxide. The nitric oxide is rapidly consumed by reaction with *isopropyl* radicals. We have trapped out a yellow solid (presumably 2-nitrosopropane) which melts at about -85°C . to

Proton Acceptor Properties of Deeply Coloured Cyclopentadiene Polymers

Cyclopentadiene can be converted catalytically, by trichloroacetic acid, into a brown-red polycyclopentadiene-trichloroacetic acid ester, (I), the colour of which is due to conjugated double bonds¹. If this ester is brought into contact with sufficiently concentrated strong acids, a dark blue, almost black, molecular compound, (II), is immediately formed. In tests in which the concentrations are small, or in which weaker acids are used, the colour of this compound is greenish-blue or green.

The reversible reaction:



has now been investigated quantitatively, (HA) being the three chloroacetic acids. Hydrochloric, sulphuric and β -naphthalene sulphonic acids were also tested, but were found to be unsuitable for quantitative measurements because the solubilities in appropriate solvents were too low. The equilibrium constant, K , of reaction (1) can be represented by the surprisingly simple relationship:

$$K = \frac{[\Sigma x_r]}{[\Sigma(P_r - x_r)] [HA]} = \frac{D_{I+II} - D_I}{(D_{II} - D_I + D_I) [HA]} \quad (2)$$

where $[\Sigma x_r]$ and $[\Sigma(P_r - x_r)]$ are the equilibrium concentration of (II) and (I), $[HA]$ is the concentration of the chloroacetic acid (which was always much greater than $[I]$), D_{I+II} is the optical density of a mixture of (I) and (II), D_{II} is the optical density at an acid concentration sufficiently high to convert all the polymer into (II), and D_I is the optical density in the absence of acid. The validity of equation (2) has been established by many experiments in the concentration-range shown in columns 2 and 3 of the accompanying table, light of 700 m μ being used for the determination of the optical densities. It has also been established at 15° , 20° and 37° and with nitrobenzene as solvent.

RESULTS OF EQUILIBRIUM AND ELECTRICAL CONDUCTIVITY MEASUREMENTS; BENZENE SOLUTION, 25.0°

	Conc. range of equilibrium tests		K (l./gm.-mol.)	Conc. range of II in conductivity tests* (10^4 number average gm.-mol./l.)	$\Lambda \times 10^4$ (ohm $^{-1} \times \text{cm.}^2/\text{number average gm.-mol.})$
	Acid (gm.-mol./l.)	Polymer (10^4 number average gm.-mol./l.)			
Cl_3CCOOH	0.0435-2.44	0.690-8.28	8.1 ± 1	29.2-59.2	7.9-39
Cl_2HCCOOH	0.155-6.05	0.828-8.28	0.82 ± 0.13	12.9-30.9	24-75
ClH_2CCOOH	0.325-1.56	5.40	0.028 ± 0.006	1.07-2.62	160-500

* In these measurements (HA) was varied in the range 0.1-1.6 gm.-mol./l. Results of tests at other concentrations will be given elsewhere.

form a yellow-brown liquid. This liquid speedily changes to a white solid at this temperature. The solid contains both nitroso and oxime groups⁴ and exhibits absorption spectra characteristic of acetoxime and a nitroso compound⁵. The ethereal solution is blue, the colour rapidly fading. A series of papers on the reaction of nitric oxide with this and other free alkyl and aryl radicals will be submitted elsewhere for publication.

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Feb. 25.

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² Küchler and Theile, *Z. phys. Chem.*, **B42**, 359 (1939).

³ Coe and Doumani, *J. Amer. Chem. Soc.*, **70**, 1516 (1948).

⁴ Feigl, "Spot Tests", 267 and 290 (Amsterdam, 1939).

⁵ Braude, *Ann. Rep. Chem. Soc.*, **42**, 112 (1945).

On plotting $\log K$ (K in fourth column of table) against the logarithm of the dissociation constants of the three chloroacetic acids in water, a linear relationship of the Brønsted type holds, which is compatible with the supposition that (I), owing to the π -electrons of the conjugated double bonds, is a proton acceptor², and that (II) is a salt. A proton transfer mechanism in the formation of these deeply coloured molecular compounds is consistent with the observation that relatively strong proton acceptors such as piperidine, dioxane, ethyl alcohol or acetone prevent the formation of (II); no such 'inhibition' occurs with polar aprotic solvents, for example, nitrobenzene or chloroform. This mechanism is proved by the marked electrical conductivity of dry benzene solutions containing (II), control experiments having established that the electrical conductivity of a benzene solution containing either (I) or (HA) alone is not significant. The 'molar' electrical conductivities, Λ , of (II), relating to the specified concentration-range, are