

Catalysis in the Exchanges of Organic Compounds with Heavy Oxygen Water

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Lifetime of Free CN Radical

By use of a method similar to that described by Oldenberg¹ for his work on OH radicals, the 0,0 band of the $^2\Sigma-^2\Sigma$ system of CN radical at $\lambda 3883$ has been observed in absorption at temperatures not far above room temperature. An absorption tube, 150 cm long and 3 cm in diameter was mounted in front of the slit of the 21-foot grating with a tungsten projection bulb behind it as the source of continuous spectra. Cyanogen at low pressure was kept flowing in the tube, and at intervals a discharge was passed through it. The discharge was controlled by a switch mounted on the same shaft with an optical shutter in front of the slit. This cut out all emission from the cyanogen discharge and passed only a short flash of the continuous background. The time between the cut-off of the discharge and this flash was regulated by the angle between the opening of the switch and the open sector in the shutter.

A cylindrical quartz lens was used to increase the speed of the grating as recommended by Oldenberg.² Intensity marks were photographed on each plate, using a calibrated step weakener. Microphotometer traces were made of the plates, and from them the relative concentrations of CN radicals were determined for different times after the end of the discharge. To eliminate possible errors in intensities due to poor resolution of the band lines the concentrations were calculated by a method based on the comparison of lines of equal intensities in the different exposures.

The concentrations were observed to fall off approximately linearly with time at pressures below one millimeter, indicating a reaction on the walls of the tube with a rate limited by the rate of diffusion to them. At higher pressures the results are still inconclusive. The rotational temperature of the absorbing gas ranges from 500° to 300°K depending on the time after the discharge. The longest life observed was six-thousandths of a second. Further experiments at higher pressures are in progress. It is expected that the observed lifetime will increase, and that a homogeneous mechanism of recombination will appear.

JOHN UNDERHILL WHITE

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University of California,
Berkeley, California,
March 19, 1938.

¹ O. Oldenberg, J. Chem. Phys. **3**, 266 (1935).

² O. Oldenberg, J. Opt. Soc. Am. **22**, 441 (1932).

Catalysis in the Exchanges of Organic Compounds with Heavy Oxygen Water*

Recent tests¹ of the exchanges of alcohols, aldehydes, ketones, esters and phenols with H_2O^{18} have demonstrated that, in the absence of a catalyst, exchange of oxygen takes place only with aldehydes, ketones, and trichloroacetic acid. Since the exchange reactions of ketones have been shown to be both general acid and hydroxyl ion catalyzed² we have performed exchange experiments with a number of organic compounds under conditions of acid and basis catalysis.

The mass spectrograph was used to determine isotopic ratios, the procedure being that of Cohn and Urey. For recovery of the water for analysis in all experiments, fractional distillation was used; in the acetic acid experiment a preliminary addition of metallic sodium was necessary. Methyl alcohol was used as a mutual solvent for the heavy oxygen water and nitrobenzene.

The results are given in Table I.

TABLE I.

SUBSTANCE	CATALYST	TIME (HR.)	TEMP. °C	NUMBER OF OXYGENS EXCHANGED
Methyl alcohol	0.1N HCl	24	25	0
Methyl alcohol	0.1N NaOH	48	25	0
Nitrobenzene	0.03N HCl	24	25	0
Nitrobenzene	0.03N NaOH	24	25	0
Potassium acetate		48	25	0
Acetic acid	0.1N HCl	40 days	25	2
Benzoic acid		4 hr.	100	2
Benzoic acid	0.1N HCl	4 hr.	100	2

The exchange of acetic acid in the presence of 0.1N HCl is especially significant when compared with the negative result obtained by Cohn and Urey for butyric acid in neutral solution. It seems probable that in general the exchange reactions of carboxylic acids are acid catalyzed; the exchange of benzoic acid in the absence of HCl may be due to the larger rate of exchange of this compound under the influence of its own acidity.

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New York, N. Y.,
April 14, 1938.

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¹ Cohn and Urey, J. Am. Chem. Soc. **60**, 679 (1938); Herbert and Lauder, Trans. Faraday Soc. **34**, 432 (1938).

² Cohn and Urey, reference 1; Roberts and Urey, J. Am. Chem. Soc. **60**, 880 (1938).