the reaction between S_2Cl_2 and NH_4Cl (described above) could be isolated in a pure state by rapidly removing the reaction flask, closing the open end of the air condenser, and then quickly replacing the drying tube with a connection to the vacuum line. By evacuating the tube and pumping for approximately 30 min. the volatile impurities were removed. The $S_3N_2Cl_2$ was scraped from the inside of the air condenser in a "dry bag" flushed with dry nitrogen. All operations involving $S_3N_2Cl_2$ should be made in a dry atmosphere, since the compound is very sensitive to atmospheric moisture; yield approximately 14 g.

Anal. Calcd. for $S_3N_2Cl_2$: S, 49.29; N, 14.36; Cl, 36.34. Found: S, 49.0; N, 14.27; Cl, 36.64; m.p. (sealed tube) 90–92°. The compound is not stable for prolonged periods even in a dry atmosphere, but may be kept for about 10 days without serious decomposition.

When 5.35 g. of ammonium chloride was refluxed with 35 ml. of S_2Cl_2 for 36 hr. in the manner described above, all the ammonium chloride was consumed and a solution of sulfur in S_2Cl_2 remained. No $S_3N_2Cl_2$ was formed in the air condenser. In a reaction similar to the above, but in which 6.4 g. of elementary sulfur was added to the reactants, crystals of $S_3N_2Cl_2$ began to form after 1.5 hr. of refluxing.

Thermal Decomposition of S_3N_2Cl.—Dark green S_3N_2Cl (1.95 g.) was prepared by thermal decomposition of $S_3N_2Cl_2$. *Anal.* Calcd. for S_3N_2Cl: N, 17.54; Cl, 22.24. Found: N, 17.95; Cl, 21.80. The S_3N_2Cl was thermally decomposed *in vacuo* at 130–150°. The volatile products (0.65 g.) were collected in a −78° trap and were identified by their infrared spectrum as NSCl[7] and SCl_2.[8] By allowing the trap to stand at room temperature overnight the NSCl formed the nonvolatile trimer $(NSCl)_3$ from which 0.145 g. of SCl_2 was readily separated. The solid nonvolatile residue from the pyrolysis was bright yellow S_4N_3Cl (1.03 g.).

Acknowledgment.—This research was supported by the U. S. Atomic Energy Commission.

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CONTRIBUTION FROM THE ROHM & HAAS COMPANY, REDSTONE ARSENAL RESEARCH DIVISION, HUNTSVILLE, ALABAMA

Isolation and Storage of Free Radicals on Molecular Sieves. I. The Electron Paramagnetic Resonance Spectrum of Nitrogen Dioxide

BY CHARLES B. COLBURN, RAYMOND ETTINGER, AND FREDERIC A. JOHNSON

Received June 21, 1963

While it has been observed that Linde Molecular Sieves can be used to store numerous materials—amines, organometallic compounds, peroxides, etc.,[1] the use of molecular sieves for the isolation and storage of free radicals has not been reported previously.

Figure 1 is the derivative e.p.r. spectrum of NO_2 adsorbed in or on Linde Molecular Sieve 13X in equilibrium with the gas phase at 750 mm. pressure of $N_2O_4 \rightleftarrows 2NO_2$. The spectrum is seen to consist of three very well defined, slightly overlapping lines. The N^{14} splitting is 56.9 gauss and the over-all width (between points of maximum slope) is 125 gauss. The individual components have widths of about 8–10 gauss, the center line being slightly narrower than the outside peaks. Our measured N^{14} interaction agrees with the isotropic interaction term derived by Atkins, *et al.*,[2] from the spin-resonance spectrum of NO_2 trapped in ice at 77°K. The *g*-value was found to be 2.003, but the influence of the "sieve" on the applied magnetic field has yet to be characterized. From the amplitude of the e.p.r. signal, we estimate the NO_2 concentration in the 13X sieve to be 10^{-5} to 10^{-4} *M*.

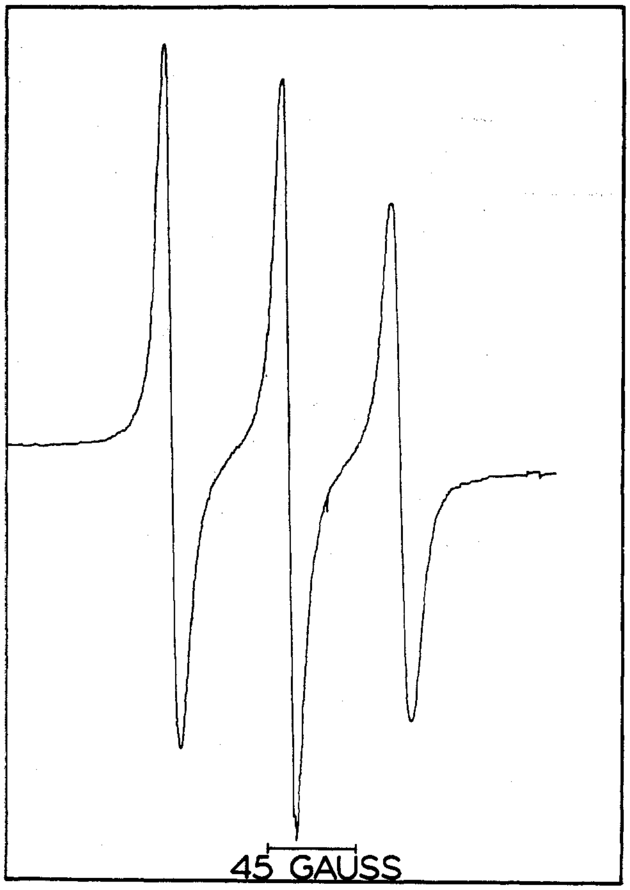

Fig. 1.—Derivative e.p.r. spectrum of NO_2 on Linde Molecular Sieve 13X. Pressure of $N_2O_4 \rightleftarrows 2NO_2$ in the gas phase over the sieve is 750 mm.

By way of comparison, the results of other investigations may be summarized. The e.p.r. spectrum of gaseous NO_2 at 5–10 mm. pressure consists of three overlapping lines, arising from coupling with the N^{14} moment. As the pressure is further decreased and collisional broadening reduced, these lines are split into a large number of components due to interaction with the molecular rotation.[3] At high pressures approaching 1 atm. and in liquid N_2O_4 (NO_2), only a single very broad line is ordinarily obtained.

The broadening of the e.p.r. signal at ordinary gas pressures may be further explained by an extremely rapid radical recombination rate to form the dimer N_2O_4; *i.e.*, the radical has a mean lifetime which is much less than 1 μsec. This effect (uncertainty broad-

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ening) is presumably operative in NO_2 solutions, for Atkins, *et al.*,[2] report that their attempts to resolve a single very broad line in such solutions have failed despite variation of temperature, concentration, and solvent over a wide range. Attempts by them to obtain rigid solutions of NO_2 by rapid cooling in liquid nitrogen have also failed, probably because dimerization was complete. On the other hand, NO_2 has been observed, while trapped in various inert matrices at low temperature (ref. 2 and other work cited therein) in which molecular rotation is largely quenched.

Adsorption on the Linde 13X sieve presumably takes place in the intracrystalline voids, comprising about half the total volume, which are connected by circular openings or pores. The resolution of the e.p.r. signal shown in Fig. 1 is ascribed to the relative isolation of the radicals (as in the dilute gas or inert solid matrix), and, in all probability, to a decreased dimerization rate. The relatively sharp lines and simple nature of the spectrum indicates that the NO_2 molecules are rotating freely while "adsorbed" in the cavities of the molecular sieves at 25°. These alkali metal aluminosilicates would appear to offer certain advantages for e.p.r. spectral studies of gaseous stable (and transitory?) free radicals. Those pressure-dependent factors which tend to broaden gaseous spectra under ordinary conditions are apparently diminished or eliminated with the technique of sieve adsorption. Also, the isotropic patterns readily obtained with the sieves can complement and confirm data derived from generally anisotropic solid matrix spectra.

NO_2 is adsorbed by both Linde Molecular Sieves 13X and 10X. The e.p.r. signal of the NO_2 on the 10X is complicated by an apparently inherent e.p.r. signal in the 10X sieve. No NO_2 signal is obtained from NO_2 on Linde Molecular Sieves 3A, 4A, or 5A. These results are consistent with the relative size of pores and cavities in these sieves.

Care must be taken to remove nearly all adsorbed water from the sieves to prevent reaction between the water–N_2O_4–NO_2 and sieve. In general, the sieves are heated to 300° with evacuation prior to the introduction of NO_2.

The adsorption of other free radicals by molecular sieves is under active investigation in these laboratories and preliminary results indicate that such adsorption may be a fairly general phenomenon.

The e.p.r. spectra reported herein were obtained with a Varian V-4502 e.p.r. spectrometer system employing 100 kc./sec. modulation and detection. The sample cells are 5 mm. o.d. and 7 in. long capped by side arms and a Fischer–Porter[4] pressure valve for loading of the cells with gas and sieve.

Caution.—Some gases will react with various molecular sieves—a rapid pressure build-up occasionally results in the bursting of the sample tube. Specifically, tetrafluorohydrazine, when adsorbed on Molecular Sieves 5A and 13X, exploded at room temperature on two different occasions.

Acknowledgment.—The authors wish to express their appreciation to Mr. William Hedges for obtaining the e.p.r. spectra reported herein. This work was performed under contract No. DA-01-021 ORD-11878.

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[4] Fischer & Porter Company, Hatboro, Penna.

CONTRIBUTION FROM THE GOVERNMENT
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The Reaction of Ruthenium Tetroxide with Pyridine

BY YOSHIO KODA

Received July 8, 1963

The addition compound of ruthenium tetroxide and pyridine having the composition $RuO_4 \cdot 2C_5H_5N$ has been prepared and some of its properties determined. The existence of this compound is not unexpected in view of the report of $OsO_4 \cdot C_5H_5N$ and $OsO_3 \cdot 2C_5H_5N$ by Criegee, *et al.*,[1] and $CrO_3 \cdot 2C_5H_5N$ by Sisler, *et al.*,[2] and of the expected Lewis acid character of ruthenium tetroxide.

An aqueous solution of ruthenium tetroxide obtained by distillation from the acid reaction mixture in which it is formed was extracted with carbon tetrachloride.[3] To the resulting carbon tetrachloride solution, cooled in an ice bath, was added a carbon tetrachloride solution of pyridine. An immediate and rapid formation of brown, needle-like crystals occurred; these gradually changed to greenish black crystals with a concurrent increase in the weight of the crystals. After 10 hr., the crystals were filtered, washed with carbon tetrachloride, and dried under vacuum.

The mole ratio of pyridine to ruthenium tetroxide in the crystals remained constant at 2:1 while the mole ratio of these two constituents in the reaction solution was varied from 1:1 to 4:1. The crystals were analyzed by thermal decomposition in a stream of hydrogen to yield a residue of ruthenium metal and by reaction with aqueous potassium hydroxide to yield the pyridine constituent.[4]

Anal. Calcd. for $RuO_4 \cdot 2C_5H_5N$: Ru, 31.1; C_5H_5N, 48.9. Found: Ru, 29.6; C_5H_5N, 48.6.

$RuO_4 \cdot 2C_5H_5N$ is insoluble in carbon tetrachloride, chloroform, benzene, and acetone, but dissolves in water, alcohol, acetic acid, and pyridine to give greenish black solutions. Its spectrum has broad absorption bands at 257 (weak), 420, and 720 mμ. The color of the aqueous solution is so intense as to be observable in concentrations as low as 2 p.p.m. The aqueous solu-

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