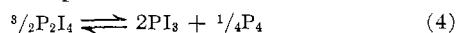


minimum. This observation probably is due to the formation of the colored intermediate ( $PI_3$ ). Hence, it would appear that the reactions actually studied were (1) and (2), principally the former. Our rate data in  $CS_2$ , as well as the qualitative data in  $CCl_4$ , would support this conclusion. For the latter, the rate of disappearance of the iodine reported by Wyllie<sup>1</sup> was of the same order as that calculated from the rate of formation of  $PI_3$  in  $CCl_4$  at 25° measured spectrophotometrically.

**Evidence for Equilibria in Solution.**— An investigation by spectrophotometric and <sup>31</sup>P nmr methods on concentrated and dilute solutions of  $PI_3$  and  $P_2I_4$  has shown that rapid equilibria do exist. A detailed study of these equilibria is complicated by the formation of poorly characterized insoluble material. Moreover, these solutions are unstable with respect to the formation of colloidal dispersions.

For the nmr study on solutions of  $P_2I_4$ , a fresh sample was prepared and slowly crystallized from a  $CS_2$  solution containing 14% excess white phosphorus. The material was washed with cold  $CS_2$  and recrystallized again from  $CS_2$ . A <sup>31</sup>P nmr spectrum was obtained on a 0.31 M solution, and the initial spectrum taken within 5 min showed the presence of small amounts of  $PI_3$  and  $P_4$  in the phosphorus atom ratio of 2:1. The phosphorus atom ratios obtained from this experiment are consistent with the equation



After approximately 0.5 hr, traces of insoluble red material began to separate from the previously clear orange solution. Identical results were obtained on a once recrystallized sample.

Additional evidence in support of the above equilibrium (eq 4) was obtained from spectrophotometric measurements. We have found that when  $P_2I_4$  was dissolved in cyclohexane or carbon tetrachloride, the characteristic spectrum of  $PI_3$  was observed. As has been shown in the Experimental Section  $PI_3$  has three characteristic maxima in the ultraviolet region in cyclohexane, while no spectrum was observed for  $P_2I_4$ . Upon standing, these dilute solutions decomposed into iodine and a phosphorus-containing colloid. The only absorption exhibited in the ultraviolet region can be attributed to iodine. Also, there was a noticeable increase in the over-all absorption, as one would expect for the presence of colloidal material.

Additional evidence for the tendency of  $P_2I_4$  to undergo disproportionation has been observed<sup>7</sup> in the reaction of  $AlI_3$  and  $P_2I_4$ . The adduct  $2PI_3 \cdot AlI_3$  and polymeric materials containing iodine, aluminum, and phosphorus were found in addition to the adduct  $P_2I_4 \cdot AlI_3$ . Polymeric materials were also observed by Moeller and Huheey<sup>5</sup> in connection with their investigation of the reaction of  $P_2I_4$  with alcohols, phenol, and amines.

When pure  $PI_3$  was dissolved in dry cyclohexane in a nitrogen atmosphere, the ultraviolet spectrum exhibited three absorption maxima, *i.e.*, 374, 287, and 223 m $\mu$ . Upon standing, this solution gave the char-

(7) M. Baudler and G. Wetter, *Z. Anorg. Allgem. Chem.*, **329**, 3 (1964).

acteristic iodine color, as evident from absorption at 520 m $\mu$ . The increased absorption at 520 m $\mu$  was accompanied by a concurrent decrease in the absorption of the three maxima attributed to  $PI_3$ . The possibility of the  $I_2$  resulting from oxidation by oxygen must be considered in any interpretation of the above observations. However, similar results were obtained on solutions which were rigorously protected from oxygen with helium and scrubbed with the latter in order to expel any dissolved oxygen. In spite of these precautions, it is still possible that the system contained small amounts of residual oxygen.

Excluding the possibility of oxidation by oxygen, the following equilibrium could account for the iodine produced in this system.



Confirmation of eq 5 is difficult since <sup>31</sup>P nmr measurements indicate that the equilibrium greatly favors  $PI_3$ , and also the existence of  $P_2I_4$  was not established by spectroscopic methods. In addition, the decomposition of  $PI_3$  in dilute solutions is rapid, particularly when exposed to ultraviolet or visible light. A possibility does exist that  $PI_3$  and/or  $P_2I_4$  are in equilibrium with  $P_4$  and  $I_2$  which would result in the catalytic conversion<sup>8</sup> of the white phosphorus into red phosphorus. The latter would be free to react with the iodine in solution to form phosphorus-iodine polymers. Polymeric material may also result from polymerization of other intermediates not observed by the techniques employed in this study.

The reaction of  $PI_3$  with glacial acetic acid at 80° followed by <sup>31</sup>P nmr offers additional support for eq 5 since the main products of the reaction are  $P_2I_4$  and  $H_3PO_4$ . These results are consistent with the initial reaction of  $PI_3$  with  $CH_3CO_2H$  to give  $H_3PO_3$  which is oxidized by  $I_2$  to  $H_3PO_4$ . The removal of the  $I_2$  results in a driving force for the buildup of  $P_2I_4$ . The catalytic decomposition by diethyl ether of  $PI_3$  to  $P_2I_4$  and  $I_2$  has been reported by Feshchenko and Kirsanov.<sup>9</sup> They reported that, at 20°, 71% conversion occurs in 7 hr. Catalysis by dioxane was also reported, but to a lesser extent.

(8) T. W. DeWitt and S. Skolnik, *J. Am. Chem. Soc.*, **68**, 2305 (1946).

(9) N. G. Feshchenko and A. V. Kirsanov, *Zh. Obshch. Khim.*, **30**, 3041 (1960).

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## Preparation and Reactions of Potassium Nitrobenzenide

BY GLEN A. RUSSELL AND ALAN G. BEMIS<sup>1</sup>

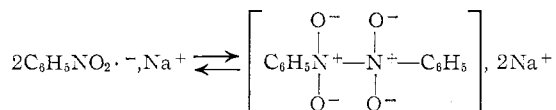
Received August 5, 1966

The reaction of deficient quantities of sodium with nitrobenzene in solvents such as tetrahydrofuran yields

(1) National Science Foundation Predoctoral Fellow, 1964-1966.

solutions containing the nitrobenzene radical anion,  $C_6H_5NO_2 \cdot^-$  (the nitrobenzenide ion), which has been unequivocally identified by esr spectroscopy.<sup>2</sup> The radical anion is readily produced by reduction of nitrobenzene in acetonitrile and other solvents at a mercury-pool electrode.<sup>3</sup>

Reaction of an excess of sodium with nitrobenzene in ether or liquid ammonia is reported to yield the disodium salt of phenylhydroxylamine,  $C_6H_5N(Na)O(Na)$ ,<sup>4</sup> and in ether either the disodium salt of nitrobenzene,  $C_6H_5NO_2Na_2$ ,<sup>5</sup> or a dimer of the monosodium salt,  $(C_6H_5NO_2)_2Na_2$ .<sup>5</sup> The possible equilibrium between the monomeric salt and the dimeric salt



is reminiscent of sodium hydronitrite ( $2Na_2NO_2 \rightleftharpoons Na_4N_2O_4$ ) formed by reaction of sodium with sodium nitrite in liquid ammonia solution.<sup>6</sup> In the case of sodium hydronitrite, magnetic susceptibility measurements have shown the solid to be 10–20% monomeric and the remainder to be the diamagnetic dimer.<sup>7</sup>

Potassium (1 g-atom) reacts with nitrobenzene (1 mole) in dry, deoxygenated tetrahydrofuran to yield a finely divided reddish solid which can be collected by filtration under nitrogen to give a light brown powder after evacuation. The infrared spectrum of the solid dispersed in potassium bromide is shown in Figure 1.

formed on a freshly prepared solvent-free sample of the solid. The results were consistent with a composition of  $72 \pm 7\%$  of monomeric potassium nitrobenzenide and  $28 \pm 7\%$  of the diamagnetic dimer. The solid had an intense esr signal which did not show fine structure. Upon standing under nitrogen for several days, the strength of the esr signal decreased considerably. The freshly prepared solid could be dissolved in dimethyl sulfoxide to give the characteristic spectrum of nitrobenzene radical anion (54 lines).<sup>8</sup> The strength of the esr signal was roughly in accord with a quantitative conversion of starting nitrobenzene to nitrobenzene radical anion.

Both the tetrahydrofuran slurry and the dimethyl sulfoxide solution of potassium nitrobenzenide react vigorously with oxygen to produce a yellowish solution containing a yellow precipitate, identified as potassium superoxide. The solutions contained appreciable amounts of nitrobenzene. A slurry of potassium nitrobenzenide prepared from 3.26 mmoles of nitrobenzene and 3.33 mg-atoms of potassium was injected by hypodermic syringe and shaken in a closed system with oxygen. Oxygen (3.18 mmoles) was consumed in a few seconds. Analysis of the tetrahydrofuran solution by gas-liquid partition chromatography showed the presence of 2.59 mmoles of nitrobenzene. No other reaction products were detected by glpc.

The precipitate formed in the oxygenation experiment was analyzed for superoxide content by the

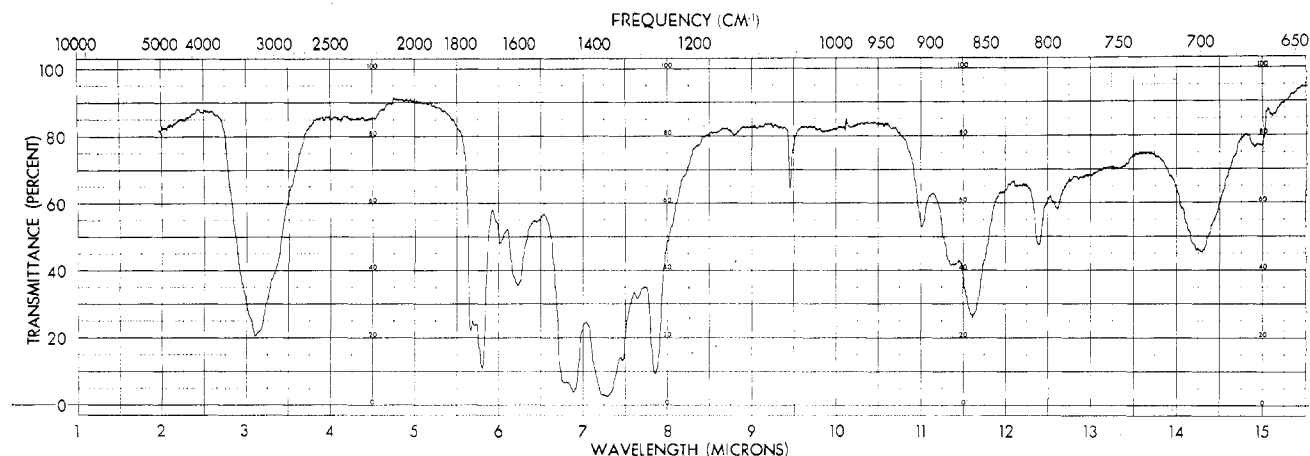


Figure 1.—Infrared spectrum of potassium nitrobenzenide in potassium bromide.

The spectrum is not similar to that of nitrobenzene in a potassium bromide disk. A solution of the solid in dimethyl sulfoxide had a  $\lambda_{max}$  at 260  $m\mu$ . Nitrobenzene in dimethyl sulfoxide gives  $\lambda_{max}$  at 265  $m\mu$ .

Magnetic susceptibility measurements were per-

(2) T. L. Chu, G. E. Pake, D. E. Paul, J. Townsend, and S. I. Weissman, *J. Phys. Chem.*, **57**, 504 (1953); R. L. Ward and M. P. Klein, *J. Chem. Phys.*, **28**, 518 (1958); **29**, 678 (1958); R. L. Ward, *ibid.*, **30**, 852 (1959).

(3) D. H. Geske and A. H. Maki, *J. Am. Chem. Soc.*, **82**, 2671 (1960).

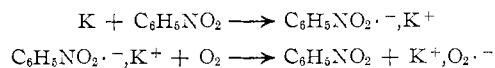
(4) J. Schmidt, *Ber.*, **32**, 2911 (1899); G. F. White and K. H. Knight, *J. Am. Chem. Soc.*, **45**, 1780 (1923).

(5) V. O. Luckashevich, *J. Gen. Chem. USSR*, **11**, 1007 (1941); *Chem. Abstr.*, **40**, 1150 (1946).

(6) E. B. Maxted, *J. Chem. Soc.*, **111**, 1016 (1917); E. Zintl and O. Kohn, *Ber.*, **61**, 189 (1928).

(7) R. W. Asmussen, *Acta Chem. Scand.*, **12**, 568 (1958).

procedure of Seyb and Kleinberg,<sup>9</sup> both as a slurry in tetrahydrofuran and as an isolated dry solid. The oxygen evolution of the tetrahydrofuran slurry indicated the presence of 2.89 mmoles of potassium superoxide ( $KO_2$ ). The experimental stoichiometries are consistent with the following reaction sequence.



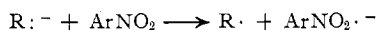
Potassium nitrobenzenide reacts readily with carbon dioxide or water to yield nitrobenzene as a major prod-

(8) G. A. Russell and S. A. Weiner, *J. Org. Chem.*, **31**, 248 (1966).

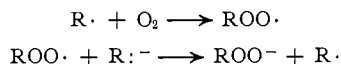
(9) E. Seyb and J. Kleinberg, *Anal. Chem.*, **23**, 115 (1951).

uct. These and further reactions of potassium nitrobenzenide are being examined.

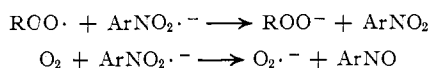
The observed reaction of the nitrobenzene radical anion with oxygen is consistent with the powerful catalytic effect observed for nitroaromatics in oxidations of carbanions such as the fluorene anion ( $R^-$ ).<sup>10</sup> By esr techniques in the absence of oxygen it was proven that electron transfer occurred.



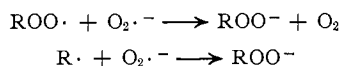
In the presence of oxygen it was found that approximately 25 molecules of fluorene were consumed for each electron-transfer step, presumably by a chain process.<sup>11</sup>



Since the efficiency of the nitroaromatic catalysts does not appear to decrease with time, we conclude that the nitroaromatic is regenerated. Reaction of the nitroaromatic radical anion with either (or both) oxygen and the peroxy radical may be involved.



Since superoxide ion is not formed in the oxidation of fluorene (1 mole of oxygen converts 1 mole of fluorene to 1 mole of fluorenone),<sup>10,12</sup> it follows that if the nitroaromatic is regenerated by the reaction of oxygen with the nitroaromatic radical anion, then the superoxide ion is destroyed, possibly by reaction with peroxy or alkyl radicals.



Indeed, we have never observed the formation of superoxide in a carbanion oxidation yielding oxygenated products although superoxide formation is a common occurrence in oxidative dehydrogenations in basic solution, such as the conversion of 9-fluorenol to 9-fluorenone.<sup>10b</sup>

#### Experimental Section

**Preparation of Potassium Nitrobenzenide.**—Tetrahydrofuran (THF) was purified by stirring over lithium aluminum hydride, followed by distillation. The first and last fractions were discarded.

In a 500-ml three-necked flask, equipped with a mechanical stirrer, pressure-equalized dropping funnel, and nitrogen inlet and outlet, was placed 2 g (50 mg-atoms) of freshly cleaned potassium in the form of small chunks together with 150 ml of THF. The apparatus was completely purged with prepurified nitrogen. A solution of 5 ml (49 mmoles) of nitrobenzene in 50 ml of THF was added slowly to the stirred mixture of potassium and THF. A brown-red, finely divided powder slowly separated from the surface of the potassium. After 2 hr the potassium had been consumed and the total volume of the solution reduced to  $150 \pm 2$  ml by vaporization of THF. The product was so finely divided

that it yielded a homogeneous-appearing slurry after stirring that could be easily pipetted. Samples of this slurry were removed from the flask by a syringe for further study.

The slurry of potassium nitrobenzenide in THF was filtered in a glove bag filled with prepurified nitrogen. Approximately 15 hr was required for the filtration. The solid obtained was dark red but became light brown after removal of all traces of solvent under vacuum. The solid could also be obtained by washing the slurry with dry, deoxygenated benzene followed by centrifuging and evacuation. The solid decomposed above 125°. The solid could be exposed to air for short periods of time without extensive decomposition.

**Oxidation of Potassium Nitrobenzenide.**—A 10-ml aliquot of the THF slurry was injected through a rubber septum into an empty 125-ml creased flask filled with oxygen and connected to a gas buret with a mercury leveling bulb and manometer. The flask was mechanically shaken<sup>10b</sup> after the slurry had been injected. The slurry gave a net gas absorption (749 mm, 27°) of 44.8 ml in 0.6 min and a total net absorption of 45.2 ml. Injection and shaking of 10 ml of THF under identical conditions produced a volume increase equivalent to 35.0 ml. Hence, the slurry actually absorbed 79.8 ml of oxygen in 0.6 min and 80.2 ml of oxygen total.

After oxygen absorption had ceased, the flask was cooled to 0° and 5 ml of diethyl phthalate was added. The contents of the flask were stirred and 10 ml of acetic acid (80%)-diethyl phthalate (20%) was added from a dropping funnel. A net evolution (corrected) of 36.3 ml of oxygen (749 mm, 27°) was observed. Slightly lower values for oxygen evolution were obtained by treatment of the filtered (*t*-butyl alcohol washed), dry precipitate obtained by oxidation. The amount of potassium superoxide present was calculated on the basis of the evolution of 1 mole of oxygen per mole of superoxide.<sup>9</sup>

When the analysis for superoxide was complete, the contents of the reaction flask were added to water and the aqueous solution was extracted with three portions of ether. The ether extracts were combined, dried, and concentrated.  $\alpha$ -Bromonaphthalene was added as an internal standard and the solution was analyzed for nitrobenzene by glpc on a 1% SE-30 silicone column at 128°. Appropriate correction factors were measured and applied for the calculation of the yield of nitrobenzene.

Any error that may have occurred in the original sampling of the THF slurry due to inhomogeneity is canceled when the results of the oxidation, superoxide analysis, and nitrobenzene recovery experiments are compared.

**Magnetic Susceptibility Measurements.**<sup>13</sup>—The magnetic susceptibility ( $\chi$ ) was determined using the mutual inductance technique<sup>14</sup> in which a weighed sample in an evacuated Pyrex tube was introduced into an inductance coil and the change in coupling due to the sample related to  $\chi$  by the equation  $\Delta M = n\chi_m\Gamma$ , wherein  $M$  is the mutual inductance,  $n$  is the number of moles,  $\chi_m$  is the molar magnetic susceptibility, and  $\Gamma$  is an instrument constant determined for the apparatus employed by calibration with manganous ammonium sulfate. The apparatus used had a sensitivity such that a  $\chi_m$  of  $10^{-8}$  emu/mole could be measured to  $\pm 1\%$ . A sample of 1.9024 g of potassium nitrobenzenide yielded a value of  $\Delta M$  (in arbitrary units) of  $0.184 \pm 0.0134$  (average of four experiments) at 77.8°K. From the measured  $\Delta M$  and the instrument constant  $\Gamma$  a value of  $\chi = 4.0 \times 10^{-5}$ /g was measured or an apparent  $\chi_m = 342 \times 10^{-5}$ . The value of  $\chi_m$  calculated from the relationship  $\chi_m = N\beta^2g^2S(S+1)/3kT$  (Curie law assumed) is  $482 \times 10^{-5}$  ( $g = 2$ ,  $S = 1/2$ ). A diamagnetic correction of  $6.2 \times 10^{-5}$  was assumed based on the reported susceptibility of nitrobenzene;  $\chi_m(\text{cor}) = 476 \times 10^{-5}$ . The sample of potassium nitrobenzenide was thus calculated to contain 72 wt % of the monomeric species at 77.8°K with an experimental uncertainty of  $\pm 7\%$ .

(10) (a) G. A. Russell, E. G. Janzen, H.-D. Becker, and F. J. Smentowski, *J. Am. Chem. Soc.*, **84**, 2652 (1962); (b) G. A. Russell, E. G. Janzen, A. G. Bemis, E. J. Geels, A. J. Moye, S. Mak, and E. T. Strom, "Oxidation of Hydrocarbons in Basic Solution," *Advances in Chemistry Series*, No. 51, American Chemical Society, Washington, D. C., 1965, p 112.

(11) G. A. Russell, *J. Am. Chem. Soc.*, **76**, 1595 (1954).

(12) Product formation involves  $R_2\text{CHOOH} + B^- \rightarrow R_2\text{CO} + \text{HB} + \text{OH}^-$ .<sup>10b</sup>

(13) We wish to thank Dr. B. C. Gerstein and Mr. F. Rioux for the magnetic susceptibility measurements.

(14) F. R. McKin and W. P. Wolf, *J. Sci. Instr.*, **34**, 64 (1957).