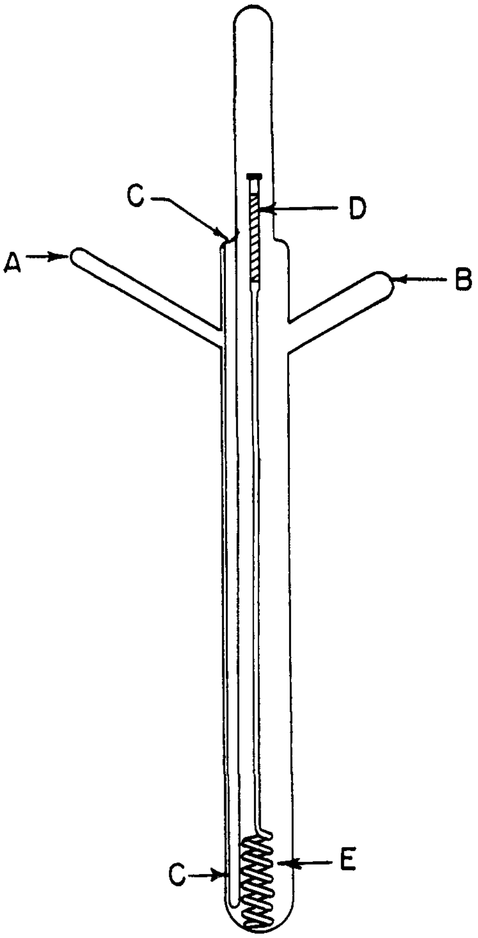


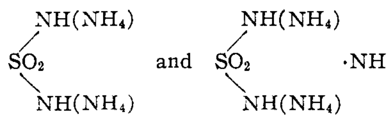
Fig. 1.—Freezing point cell.

points were each determined at least twice and are believed to be correct within 1.5°. Each portion of the curve was checked at least twice and no more than seven consecutive points were determined without cleaning out the cell completely.

The results of this phase study are represented graphically in Fig. 2. This figure indicates the formation of two previously unreported compounds, *viz.*, $SO_2(NH_2)_2 \cdot 2NH_3$ and $SO_2(NH_2)_2 \cdot 3NH_3$, with melting points of −15.8° and −12.5°, respectively. It came as something of a surprise that the 1:1 compound is not indicated. Eutectics were observed at −21.8° and 59.5 mole % of ammonia, at −19.0° and 69.1 mole % of ammonia, and at about −78.0° and about 97 mole % of ammonia.

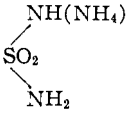
Discussion and Conclusions

The complete solvolysis of sulfamide in solution in anhydrous sulfuric acid prevents (or at least makes very difficult) the determination of whether or not sulfamide acts as a base toward sulfuric acid. With reference to the sulfamide–ammonia system, one might be tempted to interpret the formation of the compounds $SO_2(NH_2)_2 \cdot 2NH_3$ and $SO_2(NH_2)_2 \cdot 3NH_3$ as indicating that sulfamide acts as an acid toward anhydrous ammonia. The two compounds would thus be formulated



$$SO_2\begin{cases}NH(NH_4)\\NH(NH_4)\end{cases} \quad \text{and} \quad SO_2\begin{cases}NH(NH_4)\\NH(NH_4)\end{cases} \cdot NH_3$$

If this is the correct interpretation, however, it is difficult to understand why no evidence for the compound $SO_2(NH_2)_2 \cdot NH_3$, or



$$SO_2\begin{cases}NH(NH_4)\\NH_2\end{cases}$$

was obtained. There is no question, however, about the existence of the two new compounds, whatever may be the nature of their structures.

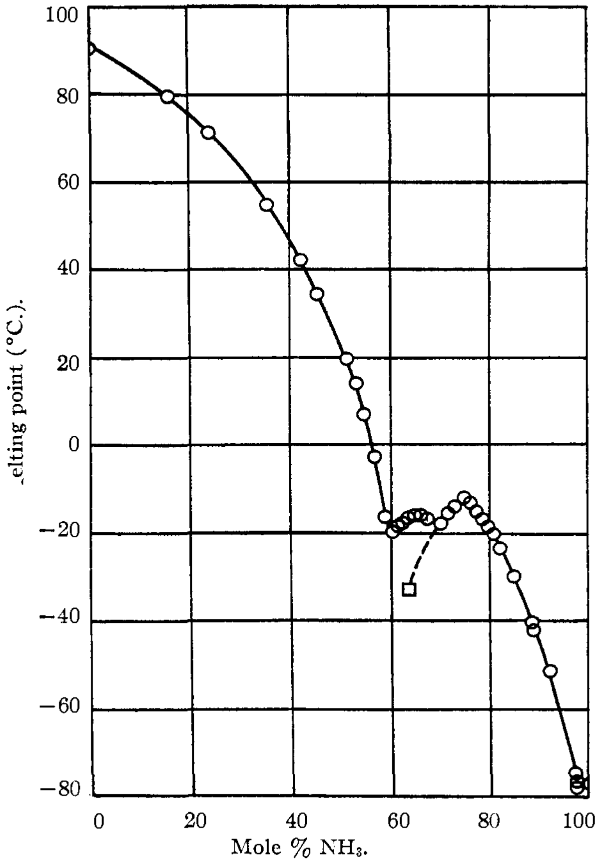


Fig. 2.—The system sulfamide–ammonia.

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Precipitate-Ion Exchange Reactions Using Nickel-63

By George K. Schweitzer and Parker B. Baum

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A number of solid–fluid exchange reactions have been carried out in the past.[1] The purpose of these experiments was to investigate the exchange of nickel(II) ions in aqueous solution with nickel(II) in a number of insoluble compounds.

Experimental

Preparation of Compounds.—The insoluble nickel(II) compounds were prepared by the procedures described in the literature references cited in the footnotes of Table I.

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[1] A. C. Wahl and N. A. Bonner, "Radioactivity Applied to Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1951, pp. 351–364.

TABLE I

EXCHANGE RESULTS

Compound	Percentage exchange in 20 min.	40 min.	60 min.	Half time (min.)	Rate
Nickel(II) orthophosphate[a]	45	67	84	23	2.3×10^{-6}
Nickel(II) pyrophosphate[b]	32	62	81	25	2.2×10^{-6}
Nickel(II) sulfide[c]	34	67	79	26	2.1×10^{-6}
Nickel(II) hydroxide[d]	33	50	70	41	1.3×10^{-6}
Nickel(II) hexacyanoironate(II)[e]	16	37	55	53	1.0×10^{-6}
Tetrapyridine nickel(II) thiocyanate[f]	10	23	35	99	6.1×10^{-7}
Bis-diphenylthiocarbazide nickel(II)[g]	10	19	27	139	4.4×10^{-7}
Bis-salicyaldoxime nickel(II)[h]	5	17	20	173	3.5×10^{-7}
Bis-dimethylglyoxime nickel(II)[i]	No exchange				

[a] R. Tupputi, *Ann. chim. phys.*, [2] **78**, 133 (1840); J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. XV, Longmans, Green and Co., New York, N. Y., 1936, p. 494. [b] A. Schwarzenberg, *Ann.*, **65**, 158 (1848). [c] N. V. Sidgwick, "Chemical Elements and Their Compounds," Vol. 11, Oxford University Press, New York, N. Y., 1950, p. 1432. [d] R. Tupputi, ref. *a*, p. 383. [e] P. Walden, *Z. physik. Chem.*, **10**, 710 (1892). [f] G. Spacu and J. Dick, *Z. anal. Chem.*, **71**, 442 (1927). [g] W. Parri, *Giorn. farm. chim.*, **73**, 207 (1924); *C. A.*, **19**, 223 (1925). [h] H. L. Riley, *J. Chem. Soc.*, 895 (1933). [i] L. Tschugaeff, *Compt. rend.*, **145**, 679 (1907).

Radioactive Nickel-63.—The radioactive nickel tracer employed was nickel-63, which emits a 0.057-Mev. beta particle with a half-life of 85 years.[2] This was obtained from the Oak Ridge National Laboratory as nickel(II) chloride in dilute hydrochloric acid.

Exchange Procedure.—All exchange reactions were carried out at 25°. Each reaction mixture consisted of 5.00 ml. of 0.0309 *M* radioactive nickel(II) chloride solution, 10.00 ml. of water and the insoluble nickel(II) compound under consideration. These were prepared by precipitating the nickel(II) ion from 4.05 ml. of 0.0381 *M* nickel(II) chloride solution. This gave equimolar quantities of nickel in the two species involved in each reaction. Reaction mixtures of each compound were vigorously stirred for periods of 20, 40 and 60 minutes. The precipitates were separated by suction filtration and the filtrates were treated with ammoniacal dimethylglyoxime solution to precipitate the nickel as bis-dimethylglyoxime nickel(II). These precipitates were mounted on fritted glass filter discs and the activity of each was measured. All samples were greater than infinite thickness for self absorption. A standard counting sample was prepared from the original radioactive solution.

Radioactivity Apparatus.—A Tracerlab SC-16 Windowless Flow Counter operating in the Geiger region was used in conjunction with a Tracerlab SC-2A Scaler to measure the activities of the samples. All samples were counted for a sufficiently long time to give a standard deviation equal to or less than 1%.

Results

The experimental results are shown in Table I. All systems except the bisdimethylglyoxime nickel(II) one showed exchange for the period of time of the reactions. Plots of the logarithm of one minus fraction exchange against time gave straight lines for all other exchange reactions. The rates of exchange were then calculated from the expression as given by Wahl and Bonner.[3] This equation is said to apply to heterogeneous reactions only if the mixing of isotopes in each phase is rapid as compared to the actual exchange process or to the diffusion across the interface.

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[2] "Isotopes," United States Atomic Energy Commission, Isotopes Division, March, 1951, p. 5.

[3] A. C. Wahl and N. A. Bonner, ref. 1, p. 34.

Dealkylation of Dialkylhydroquinone Diacetates with Aluminum Chloride[1]

BY JACK L. R. WILLIAMS

RECEIVED JULY 14, 1952

When hydroquinone diacetate is submitted to the Fries rearrangement, the product is acetylhydroquinone.[2] However, when 2,5-dimethylphenyl acetate is treated under similar conditions, 2-acetyl-4,6-dimethylphenol results.[3] The acetyl group displaces an ortho-methyl group, rather than taking the open para-position.

In the course of studying the behavior of alkylhydroquinone diacetates, it has been found that dealkylation took place in the case of 2,5-di-*t*-butylhydroquinone and 2,5-di-*t*-amylhydroquinone diacetates. The reactions were carried out using anhydrous aluminum chloride in the absence of a solvent; the products were acetylhydroquinone, instead of the expected dialkylacetohydroquinone, and much tar. The alkyl side chains were probably eliminated as the aluminum chloride complexes which would be expected to polymerize under the reaction conditions.

Experimental

2,5-Di-*t*-butylhydroquinone Diacetate.—To a mixture of 22.2 g. (0.1 mole) of 2,5-di-*t*-butylhydroquinone and 51.0 g. (0.5 mole) of acetic anhydride there was added, with shaking, 5 cc. of a solution of 5 drops of concentrated sulfuric acid in 10 cc. of acetic anhydride. The temperature rose immediately and the reaction mixture was allowed to stand for 1.0 hour, after which time it was poured into 1.0 liter of ice-water. The white crystals were filtered and dried to yield 28.8 g. (94%), m.p. 172–173°. A small sample was recrystallized from benzene and dried *in vacuo*, m.p. 173–174°.

Anal. Calcd. for $C_{18}H_{26}O_4$: C, 70.6; H, 8.6. Found: C, 71.1; H, 8.9.

2,5-Di-*t*-amylhydroquinone Diacetate.—From 25.0 (0.1 mole) of 2,5-di-*t*-amylhydroquinone and 51.0 g. (0.5 mole) of acetic anhydride there was obtained, by the above procedure, 33.0 g. (98%) of 2,5-di-*t*-amylhydroquinone diacetate, m.p. 114–115° (softened at 112–113°).

Anal. Calcd. for $C_{20}H_{30}O_4$: C, 71.8; H, 9.0. Found: C, 72.2; H, 9.4.

Rearrangement of 2,5-Di-*t*-butylhydroquinone Diacetate with Aluminum Chloride.—A mixture of 50 g. (0.16 mole)

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[1] Communication No. 1501 from the Kodak Research Laboratories.

[2] G. C. Amin and N. M. Shah, *Org. Syntheses*, **28**, 42 (1948).

[3] K. von Auwers, H. Bundesmann and F. Wieners, *Ann.*, **447**, 162 (1926).