[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF WISCONSIN]

Exchange Reactions of Some 4-Coördinated Nickel Complexes

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We have studied the exchange reactions of fourteen 4-coördinated nickel complexes of various types using labeled nickel chloride in solution at room temperature. The exchange results are correlated with published magnetic susceptibilities and other measurements indicative of the types of bonds present. All four of the compounds which are paramagnetic in the solid state exchanged readily. Five of the diamagnetic complexes did not exchange, while five others did. Ethylenediamine, as contrasted with its higher homologs, confers special inertness on certain complexes containing it. A previous correlation between rate of nickel exchange and rate of nickel precipitation with dimethylglyoxime is confirmed and extended. A comparison is made of the rate of exchange of the central atom in certain complexes of copper and of nickel.

While no completely general relation is to be expected between the strength or nature of bonds in compounds and their rates of isotopic exchange, many special correlations of this type are well established.[3-6] In particular Johnson and Hall,[7] who studied nickel complexes in solution, report "in the main ... a satisfactory correlation (of exchange rates) with predictions of bond type based on other criteria." The purpose of the present work was to survey the exchange behavior of some additional 4-coördinated nickel complexes and if possible to define more clearly the relationships between bond type and exchangeability of the central atom.

Experimental

Radioactive Nickel.—The radionickel used was obtained from the Isotopes Division, U. S. Atomic Energy Commission at Oak Ridge. It is probably a mixture of Ni^{63} and Ni^{59}. Both of these isotopes are long lived and give off principally very soft radiation.[8] In this paper the radionickel will be referred to as Ni^{63}, since this apparently is the predominant isotope. As received from Oak Ridge, the radionickel was contaminated by Co^{60}. This was removed by adding cobalt carrier and precipitating the nickel with dimethylglyoxime. Three or four precipitations were usually sufficient to reduce the cobalt activity to a level which could not interfere with the counting of the radionickel.

Exchange Procedure.—A quantity of the nickel complex was dissolved in a suitable solvent, usually pyridine or methyl cellosolve. Since the complexes were slightly soluble, a nearly saturated solution was generally used, and in most cases the concentration was close to $10^{-2}M$. Approximately equivalent amounts of the solution of the complex and of a methyl cellosolve solution of radioactive nickel chloride were mixed and shaken mechanically at room temperature. After an appropriate time, the complex was separated from the salt. This was accomplished either by pouring the exchange solution into ice water to precipitate the complex, or by adding chloroform and water and extracting repeatedly, the nickel chloride going into the aqueous phase and the complex into the chloroform phase. The nickel chloride solution was evaporated to dryness to get rid of the organic solvent and the residue was taken up in sulfuric acid. The acid was neutralized, a large excess of ammonia added, and the nickel removed by electrolysis. If the complex was in chloroform solution, the organic solvent was evaporated. The complex was then treated with nitric acid and this solution was evaporated to dryness. The residue was taken up in sulfuric acid and heated. If the complex had been precipitated and filtered, it was destroyed with nitric acid, the solution was evaporated to dryness, and sulfuric acid added and heated. At this point, in either procedure, the solution was neutralized, an excess of aqueous ammonia added and the solution electrolyzed to remove the nickel.

The nickel was electroplated onto a weighed platinum foil electrode approximately 4 × 4 cm. in size. The washed electrode was then reweighed to determine the weight of the nickel. All weighings were made on a microbalance. The electrode was placed inside the ionization chamber of a Lauritsen electrode and the rate of discharge of the electroscope was measured and expressed as scale divisions per minute. The counting rate was then corrected for the background discharge rate of the electroscope. This corrected counting rate was divided by the weight of the nickel to give the specific activity of the nickel in the given fraction. In only five cases did the weight of the nickel deposit exceed 100 micrograms per sq. cm., and of these the greatest was 242 $\mu g.\ cm.^{-2}$. In 35 cases the deposit weighed less than 100 $\mu g.\ cm.^{-2}$. At these thicknesses self-absorption should not affect the specific activity within the error of the measurement.[8]

If no exchange occurs the specific activity of the nickel chloride fraction is equal to that of the original radionickel, while that of the complex fraction is essentially zero. If complete exchange occurs, the specific activities of the two fractions are equal. In other cases the extent of exchange is measured by the ratio of the specific activity of the complex to the specific activity for complete exchange calculated from the relative weights of the two types of nickel used.

Solvents.—Methyl cellosolve is an effective solvent for most of these complexes and for simple nickel salts. Since pyridine, like ammonia, forms quite stable complexes with nickel ion, it may be expected[7,9] to modify the exchange behavior of a complex more than methylcellosolve. It is also almost the only common organic solvent known to dissolve certain of the complexes. In the pyridine experiments, a mixed solvent was used for convenience, since the radionickel chloride was already in methyl cellosolve solution.

Analysis of Compounds.—All the complex salts were analyzed for nickel by the dimethylglyoxime method except that in the cases of compounds 10, 14 and 15 the residue from the carbon and hydrogen determinations was weighed and assumed to be NiO. Compounds no. 6, 7 and 14 were analyzed for C and H by the Clark Microanalytical Laboratory, Urbana, Illinois, all the others by the microanalytical laboratory of this Department. The correspondence between the analytical results calculated and found was satisfactory in all cases.

Results

The complexes studied are arranged in four groups in Table I. Some of Johnson and Hall's results are included for comparison. In the column headed Solvent, "Mecel, Etcel, Acet." and "Pyr." stand for methyl and ethyl cellosolve, acetone, and a 7–3 mixture of pyridine and methyl cellosolve, respectively. Under Separation method, "P" means precipitation by dilution with ice-water and "E" extraction into chloroform.

Discussion

Group. I. 1. Bis-(salicylaldehydo)-nickel.—Studied by Johnson and Hall.[7] Paramagnetic both in the solid state[10] and in pyridine solution.[9]

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[3] N. F. Hall and O. R. Alexander, THIS JOURNAL, **62**, 3455 (1940).

[4] *Chem. Soc. London Ann. Reports*, **38**, 89 (1941).

[5] M. Haissinsky *J. chim. phys.*, **47**, 957 (1950).

[6] C. S. Garner, "Applications of Exchange Reactions in Studying Lability" (paper presented at the Symposium on Equilibrium and Rate Behavior of Complex Ions in Solution), Chicago, Ill., February 21, 1951.

[7] J. E. Johnson and N. F. Hall, THIS JOURNAL, **70**, 2344 (1948).

[8] A. R. Brosi, Č. J. Borkowski, E. E. Conn and J. C. Griess, Jr., *Phys. Rev.*, **81**, 391 (1951).

[9] J. B. Willis and D. P. Mellor, THIS JOURNAL, **69**, 1237 (1947).

[10] G. N. Tyson and S. C. Adams, *ibid.*, **62**, 1228 (1940).

TABLE I

No.	Name	Solvent	Separation method	Time of contact	Specific activity S.D./min./mg. Salt	Complex	Exchange, %
	GROUP I. COMPLEXES PARAMAGNETIC IN THE SOLID STATE AND WHICH EXCHANGED RAPIDLY IN SOLUTION						
1	Bis-(salicylaldehydo)-nickel	Mecel		5 min.			100^a
		Mecel	P	5 min.	0.341	0.338	100
		Mecel		1 hr.			100^a
2	Bis-(salicylaldehyde)-di-(γ-iminopropyl)-aminenickel	Mecel	E	10 min.	.278	.282	100
3	Bis-(salicylaldehyde)-trimethylenediiminonickel	Mecel	P^b	5 min.	.213	.190	97
4	Bis-(8-quinolinolo)-nickel	Pyr^c	P^d	5 min.	3.49	.342	99
	GROUP II. COMPLEXES DIAMAGNETIC IN THE SOLID STATE WHICH DID NOT EXCHANGE UNDER ANY OF THE CONDITIONS TRIED						
5	Bis-(salicylaldehyde)-ethylenediiminonickel	Etcel		5 min.			0^a
		Etcel		1 hr.			0^b
		Mecel	P	2 hr.	0.702	0.033	0
		Mecel	E	50 hr.	.642	.028	0
		Pyr	E	48 hr.	.708	.004	0
6	Bis-(acetylacetone)-ethylenediiminonickel	Mecel	E	2 hr.	.738	.002	0
		Pyr	E	48 hr.	.690	.003	0
7	Bis-(3-methoxysalicylaldehyde)-ethylenediiminonickel	Mecel	E	2 hr.	.768	.003	0
8	Bis-(methylbenzylglyoximo)-nickel	Acet		5 min.			0^a
		Acet		1 hr.			0^a
9	Bis-(salicylaldehyde)-*o*-phenylenediiminonickel	Mecel	P	2 hr.	.715	.048	0
		Mecel	E	44 hr.	.631	.020	0
		Pyr	E	48 hr.	.767	.005	0
10	Bis-(4-hydroxysalicylaldehyde)-ethylenediiminonickel^e	Mecel	P	2 hr.	.699	.046	0
	GROUP III. COMPLEXES DIAMAGNETIC IN THE SOLID STATE BUT WHICH EXCHANGED RAPIDLY IN SOLUTION						
11	Bis-(salicylaldimino)-nickel	Mecel		5 min.			93^a
		Mecel		1 hr.			100^a
12	Bis-(salicylaldoximo)-nickel	Mecel		5 min.			100^a
		Mecel		1 hr.			94^a
13	Bis-(N-methylsalicylaldimino)-nickel	Mecel	E	5 min.	0.377	0.371	99
14	Bis-(3-methoxysalicylaldehyde)-trimethylenediiminonickel	Mecel	E	5 min.	.332	.240	87
		Mecel	P	2 hr.	.215	.212	100
15	Bis-(salicylaldehyde)-tetramethylenediiminonickel	Mecel	E	5 min.	.464	.381	88
	GROUP IV. DIAMAGNETIC COMPLEXES WHICH EXCHANGED SLOWLY						
16	Bis-(dimethylglyoximo)-nickel	Pyr	E	20.5 hr.	0.631	0.366	63
		Pyr	P^b	48 hr.	.293	.278	98
17	Bis-(methyl-*n*-butylglyoximo)-nickel	Mecel		5 min.			0^a
		Mecel		1 hr.			0^a
		Mecel	E	48 hr.	.370	.241	82
		Pyr	E	48 hr.	.119	.116	100

[a] Results of Johnson and Hall.[7] [b] A small fraction of the complex remained in solution after the addition of water. This was removed by extraction of the filtrate with chloroform. [c] Pyridine–methyl cellosolve 1-1. [d] A small amount of NaCl was added to salt out the complex. [e] No magnetic data.

The report of Johnson and Hall that complete exchange occurred within 5 minutes is confirmed.

2. **Bis-(salicylaldehyde)-di-(γ-iminipropyl)-aminenickel.**—Paramagnetic in the solid state (3.25 Bohr magnetons).[11] If the nickel atom is 4-coördinated in this complex, the bonds are probably ionic or sp^3 covalent. 5-Coördination is also possible, with trigonal bipyramidal structure. No dipole moment or X-ray data are available to help decide this question. Complete exchange of nickel atoms was observed within ten minutes.

3. **Bis-(salicylaldehyde)-trimethylenediiminonickel).**—Barkelew[12] reported that this complex has a magnetic moment of 3.28 Bohr magnetons. Essentially complete exchange of nickel atoms occurred within five minutes in methyl cellosolve. The contrast with the ethylenediamine complexes (5, 6, 7 and 10) is noteworthy.

4. **Bis-(8-quinolinolo)-nickel.**—Since this complex has practically the same moment[9] in pyridine solution as in the solid state (3.26 and 3.2 Bohr magnetons, respectively) one would expect exchange, which in fact was found to occur completely within five minutes.

Group II. 5. Bis-(salicylaldehyde)-Ethylenediiminonickel.—Also studied by Johnson and Hall,[7] who found no exchange in ethyl cellosolve within 60 minutes. Diamagnetic both in the solid state and in pyridine solution.[9] Our test showed no exchange in methyl cellosolve, confirming the earlier work. Since for this compound the magnetic data of Willis and Mellor give no evidence of a change of bond type in pyridine solution, exchange was not expected even in this solvent. This was the result obtained. Absorption spectra were

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[11] M. Calvin and C. H. Barkelew, THIS JOURNAL, **68**, 2267 (1946).

[12] C. H. Barkelew, "Magnetic Properties of Chelate Derivatives of Salicylaldehyde," Ph.D. Thesis, University of California, Berkeley, 1944.

determined in methyl cellosolve and in pyridine solutions. They have the same general characteristics, the peaks and troughs being shifted slightly toward longer wave lengths in the pyridine. Thus, the magnetic data, the spectral data, and the exchange data all indicate that there is no change in bond type of this complex when it is dissolved in any solvent tried.

6. **Bis-(acetylacetone)-ethylenediiminonickel.**—Diamagnetic in the solid state and in chloroform and ethanol solutions[9]; no measurements in pyridine. In methyl cellosolve no exchange occurred within 2 hours. In pyridine, there was no exchange within 48 hours. The absorption spectra of this complex in methyl cellosolve and pyridine solutions are so similar that they suggest no difference in bond type.

7. **Bis-(3-methoxysalicylaldehyde)-ethylenediiminonickel.**—Barkelew[11] found this complex diamagnetic in the solid state. No data are available on its magnetic properties in solution. No exchange of nickel atoms occurred under the conditions of the experiment.

8. **Bis-(methylbenzylglyoximo)-nickel.**—Johnson and Hall found no exchange. In view of our results on the other two glyoximes (nos. 16 and 17), a further study of this complex would be desirable.

9. **Bis-(salicylaldehyde)-*o*-phenylenediiminonickel.**—Willis and Mellor[9] found that this complex is diamagnetic in the solid state, but paramagnetic to the extent of 2.55 Bohr magnetons in pyridine solution. They postulate a partial change to octahedral bonding due to the pyridine. Unfortunately, they did not determine the magnetic susceptibility of this complex in solvents other than pyridine, so it was not known whether other solvents also can cause such a change.

The results indicate that no exchange took place in methyl cellosolve solution. The small amount of activity found in the complex must be attributed to faulty separation of the two fractions. Any modification of the type of bonding of the nickel atom by this solvent is not of such nature as to permit exchange to occur. Since Willis and Mellor found that pyridine does cause a change of bond type, an exchange experiment was carried out in presence of pyridine. The results can only be interpreted to mean that there was no exchange within 48 hours. It was decided to look for other evidence of a change in bond type by comparing the absorption spectra of this complex in pyridine and methyl cellosolve solutions. It was found that pyridine causes a change in the entire character of the spectrum (see Fig. 1).

One must conclude that pyridine does indeed cause a change in the bond type of this complex. This is the only case yet observed of a nickel complex paramagnetic in solution which fails to exchange. This is hard to understand.

10. **Bis-(4-hydroxysalicylaldehyde)-ethylenediiminonickel.**—Although no magnetic data are available for this complex, it is classed in this group because it showed no exchange and is presumably (from its structure) diamagnetic in the solid state.

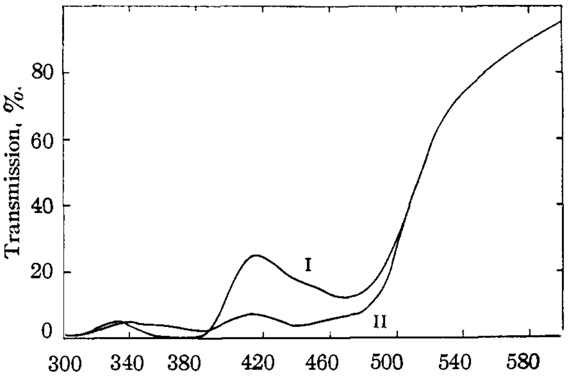

Fig. 1.—Absorption spectra of bis-(salicylaldehyde)-*o*-phenylenediiminonickel: concentration of complex 10^{-4} molar: curve I, methyl cellosolve solution; curve II, pyridine solution.

Group III. 11. Bis-(salicylaldimino)-nickel. 12. Bis-(salicylaldoximo)-nickel and 13. Bis-(N-methylsalicylaldimino)-nickel.—Of the eight 4-coördinated nickel complexes studied by Johnson and Hall, only two did not show the exchange behavior they predicted in 1941 from a consideration of the magnetic properties of the solid complexes. In both of these cases, bis-(salicylaldimino)-nickel and bis-(salicylaldoximino)-nickel, exchange was found to occur within five minutes, whereas the diamagnetism of the solid complexes has led to the prediction that exchange would not occur. In 1947, Willis and Mellor[4] reported that whereas bis-(salicylaldimino)-nickel is diamagnetic in the solid state and in benzene solution, it is paramagnetic to the extent of 1.1 Bohr magnetons in chloroform solution and of 3.1 Bohr magnetons in pyridine solution; also, bis-(salicylaldoximo)-nickel, though diamagnetic in the solid state, is paramagnetic to the extent of 2.3 Bohr magnetons in pyridine solution. This led Johnson and Hall to suggest in their paper (1948) that the covalent bonds of the diamagnetic solid compound are modified sufficiently by solvents to allow thermal exchange to occur.

Bis-(N-methylsalicylaldimino)-nickel was another of the complexes studied by Willis and Mellor who found it to have properties similar to those of bis-(salicylaldimino)-nickel and bis-(salicylaldoximino)-nickel, *viz.*, it is diamagnetic in the solid state and paramagnetic to the extent of 2.2, 2.4, 2.4, 2.3 and 3.1 Bohr magnetons in chloroform, benzene, ethanol, dioxane and pyridine, respectively. It was of interest to see if its exchange behavior was also similar.

The results show that complete exchange took place within five minutes. Apparently, in this case also, the solvent causes modification of the bonds sufficient to allow exchange.

14. **Bis-(3-methoxysalicylaldehyde)-trimethylenediiminonickel.**—The complex was prepared as the dihydrate. Heating at 80° for three hours under vacuum gave the anhydrous complex.

Anal. Calcd. for $C_{19}H_{20}O_4N_2Ni \cdot 2H_2O$: C, 52.45; H, 5.56; Ni, 13.49. Found: C, 52.39; H, 5.32; Ni, 13.24. Calcd. for $C_{19}H_{20}O_4N_2Ni$: C, 57.18; H, 5.05; Ni, 14.71. Found: C, 56.84; H, 4.91; Ni, 14.41.

Barkelew[12] found that when there are two molecules of water associated with each molecule of this complex it has a magnetic moment of 3.1 Bohr magnetons and is green in color. When this substance is desolvated, the color changes to red and it becomes diamagnetic. This indicates that the anhydrous complex is planar. When two water molecules are introduced, they presumably enter the coördination sphere of the nickel causing a modification of the bond type leaving two unpaired electrons. This probably involves the assumption by the nickel atom of an octahedral configuration with a coördination number of six.

The dihydrate, a green crystalline material, dissolved in methylcellosolve to give a brown solution. The anhydrous complex and the dihydrate gave identical absorption spectra in methyl cellosolve. This indicates that the water molecules of the dihydrate are no longer associated with the nickel ion.

The results show that the nickel atoms undergo rapid exchange under the conditions of the experiment. The exchange is complete within two hours and proceeds to the extent of 87% within five minutes. It may be that the exchange is complete within five minutes, the discrepancy being due to unknown experimental errors. This result is not surprising in view of the evidence that the presence of water in the crystal can cause a change in the magnetic properties of the substance. It is not unreasonable to suppose that the solvent can cause similar changes which permit exchange to occur.

15. **Bis-(salicylaldehyde)-tetramethylenediiminonickel.**—This complex was found by Barkelew[11] to be diamagnetic in the solid state. No data are available on its magnetic properties in solution.

The exchange experiment left something to be desired, both as to the purity of the complex used and as to the results. The results are reported because they indicate that rapid exchange has occurred, though the exact extent of the exchange is somewhat uncertain. This complex is certainly more reactive toward exchange than no. 5, 6, 7 and 10 probably because in this case the chelate bonds must form a seven-membered ring. The magnetic data indicate that the nickel is planar in the solid state. Evidently the solvent causes a modification of the bonds which is sufficient to permit exchange.

16. **Bis-(dimethylglyoximo)-nickel and 17. Bis-(methyl-*n*-butylglyoximo)-nickel.**—Sugden[13] made a study of a series of nickel glyoximes and found that they were all diamagnetic in the solid state. Willis and Mellor[9] found that a pyridine solution of bis-(dimethylglyoximo)-nickel was paramagnetic to the extent of 1.5 Bohr magnetons. This indicates that some modification of the bond type similar to that suggested for bis-(salicylaldehyde)-orthophenylenediiminonickel is probably taking place. In view of the fact that the latter was found not to undergo exchange in the presence of pyridine even after 48 hours, it was expected that bis-(dimethylglyoximo)-nickel also would not show exchange under these conditions. *The results are interpreted to mean that bis-(dimethylglyoximo)-nickel undergoes exchange at a conveniently measurable rate in the presence of pyridine.* This is perhaps surprising. It indicates that the widespread view of this compound as the most highly covalent of nickel complexes is without basis. Unfortunately, it is so insoluble in most other common organic solvents that it is impossible to carry out exchange reactions in other media. As another complex of this type, bis-(methyl-*n*-butylglyoximo)-nickel was chosen because Johnson and Hall had investigated its exchange behavior in methylcellosolve solution and also because a sample of the complex used by them was available. They found a very slight amount of activity in the complex after its separation from the exchange mixture. This was attributed to adsorption of radionickel ions from the solution onto the precipitate of the complex, and it was concluded that no exchange occurred within one hour.

It seemed possible that though Johnson and Hall found no significant exchange, a longer contact period might disclose it. The material they used was analyzed for carbon and hydrogen as a check on its purity.

Anal. Calcd. for $C_{14}H_{26}O_4N_4Ni$: C, 45.07; H, 7.03; Ni, 15.73. Found: C, 45.29; H, 7.13; Ni, 15.34.

The results show that in 48 hours the exchange is fairly complete. In the presence of pyridine also, exchange was complete within the same period. In this, as in other instances, our results indicate a greater tendency of pyridine to promote exchange as compared to methyl cellosolve. A comparison of absorption spectra in the two solvents indicates some modification of the bonds by the pyridine. The difference in behavior of these two glyoximes from that of the other (no. 8) suggests the desirability of a further study of this last. These are the only two compounds examined by us in which an observed exchange was certainly measurably slow.

Summary of Exchange Behavior

The results of this study may be summarized as follows: (1) 4-Coördinated nickel complexes paramagnetic in the solid state all exchanged readily. (2) When these complexes are diamagnetic in the solid state, they fail to exchange in solution in many cases, notably the complexes with Schiff bases where the amine constituent is ethylenediamine, and so forms a five-membered ring. Also in the case of bis-(salicylaldehyde)-*o*-phenylenediiminonickel, even though the complex is paramagnetic in solution, no exchange occurs. (3) A symmetrical and an unsymmetrical glyoxime have been found to exchange at a measurable rate. (4) Several other complexes, particularly those with Schiff bases the amine constituent of which is other than ethylenediamine, show rapid exchange in solution, though diamagnetic in the solid state. In most of these cases there is other evidence that the solvent has affected the nature of the bonds with nickel.

Precipitation with Dimethylglyoxime.

The striking correlation between exchange behavior of a given nickel complex and its behavior with

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[13] S. Sugden, *J. Chem. Soc.*, 246 (1932).

dimethylglyoxime noted by Johnson and Hall was also found with this new series of nickel complexes. A 1% ethanolic solution of dimethylglyoxime was added to a methyl cellosolve solution of the complex. All of the complexes which gave an immediate precipitate with dimethylglyoxime also showed rapid nickel exchange. Of those which did not give an immediate precipitate with dimethylglyoxime, only 3 and 17 showed exchange under any of the conditions used. Number 3 gave a precipitate with dimethylglyoxime on standing overnight. It was found to undergo rapid exchange. No. 17 was tested in both methylcellosolve and acetone solution. The methyl cellosolve solution gave no visible precipitate after one hour. However, on standing overnight, a dense precipitate formed. In the acetone solution, a precipitate was barely visible after an hour. After 80 minutes, the precipitate was clearly visible. This slow formation of a precipitate with dimethylglyoxime is interesting in view of the slow exchange this complex was found to undergo.

Comparison with Copper Complexes

Several investigators[14–17] have reported that for certain chelating groups, the copper complexes are more stable than those of nickel (however, see *C. A.*, **44**, 10567*c* (1950)). It is of interest then to compare the exchange behavior of these nickel complexes with that observed for the corresponding copper complexes by Duffield and Calvin.[17] These results are not strictly comparable because of the different solvents used, and it is conceivable that the amount of pyridine present may have a large effect. Nevertheless, the comparison is interesting. It is made in Table II.

TABLE II

EXCHANGE BEHAVIOR OF NICKEL AND COPPER COMPLEXES

	Chelating group	Exchange results Copper complex	Nickel complex
1	Salicylaldehyde	Rapid exchange	Rapid exchange
2	N-Methylsalicylaldimine	Rapid exchange	Rapid exchange
3	Salicylaldehyde-ethylenediimine	Exchanges with a half-time of 2.1 hours	No exchange after 48 hours
4	Salicylaldehyde-*o*-phenylenediimine	Very slow exchange (if any)	No exchange after 48 hours
5	Acetylacetone-ethylenediimine	Exchanges with a half-time of 37 hours	No exchange after 48 hours

This comparison seems to indicate that in cases 3, 4 and 5 above, these complexes are more inert toward exchange than are the corresponding copper complexes.

Acknowledgment.—The financial assistance of the National Research Council, which provided a fellowship for the year 1949–1950, and of the Research Committee of the Graduate School of the University of Wisconsin, which supported this research with funds supplied by the Wisconsin Alumni Research Foundation, is gratefully acknowledged. We are deeply indebted to the microanalytical group of this Laboratory for their assistance.

MADISON 6, WISCONSIN RECEIVED MARCH 14, 1951

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[14] P. Pfeiffer, H. Thielert and H. Glaser, *J. prakt. Chem.*, *N. F.*, **152**, 145 (1939).

[15] D. P. Mellor and L. Maley, *Nature*, **161**, 436 (1948).

[16] M. Calvin and N. C. Melchior, THIS JOURNAL, **70**, 3270 (1948).

[17] R. B. Duffield and M. Calvin, *ibid.*, **68**, 557 (1946).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OREGON STATE COLLEGE]

The Heats of Combustion of Some Nitrogen Compounds and the Apparent Energy of the N-N Bond[1a,b]

BY LELAND G. COLE[2a,b] AND E. C. GILBERT

The N-N and N=N bond energy terms in some substituted hydrazines and in azobenzene have been evaluated from new isothermal heats of combustion of *p*-nitroaniline, 4,4′-dinitrohydrazobenzene and hydrazobenzene. A lower mean N-H bond energy term derived from recent data on hydrazine was used in the computations and compared with similar results using the adjusted N-H bond energy term for ammonia. The N-N energy terms resulting from use of the proposed lower N-H term are self-consistent and in agreement with chemical experience. The N=N bond energy term agrees with that obtained recently for the resonance-free azoisopropane molecule. Certain assumptions involved in the reduction of experimental data obtained in this Laboratory and the experimental technique on nitrogen-containing substances were tested by redetermination of the heat of combustion of hippuric acid; the value so obtained is shown to agree with the precise value of Huffman when his value is adjusted for a subsequent change in the benzoic acid standard.

Introduction

The chemical bond energy terms[3] may be obtained for the bonds A–X and A–Y of a molecule of general type AX_aY_b with little certainty in as much as the intramolecular influences of A–Y on an assigned mean value for the energy of the A–X bond previously determined from the type molecule AX_c are not known or quantitatively predictable. Further, it is known that the A–X bonds may have c energies for the formation,

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[1] (a) Published with the approval of the Monographs Publication Committee, Oregon State College as Research Paper No. 184, School of Science, Department of Chemistry. (b) For material supplementary to this article order Document 3334 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.00 for photocopies (6 × 8 inches) readable without optical aid.

[2] (a) Based on theses submitted by Leland G. Cole in partial fulfillment of the requirements for the M.A. and Ph.D. degrees at Oregon State College. (b) Present address: Jet Propulsion Laboratory, California Institute of Technology, Pasadena.

[3] E. T. Butler and M. Polanyi, *Trans. Faraday Soc.*, **39**, 19 (1943); G. E. Coates and L. E. Sutton, *ibid.*, **43**, 1188 (1947). Also see A. D. Walsh, *ibid.*, **43**, 60 (1947) and L. H. Long and R. G. W. Norrish, *Proc. Roy. Soc.* (*London*), **187A**, 337 (1946), for a discussion of the use of the terms dissociation energy, bond energy and bond heat of formation; recently M. Szwarc and M. G. Evans, *J. Chem. Phys.*, **18**, 618 (1950), have analyzed the concepts of bonding energies and discussed this general problem in detail.