325
MASTER

Chemistry-General (UC-4)

U N C L A S S I F I E D

ISC-867

UNITED STATES ATOMIC ENERGY COMMISSION
RESEARCH AND DEVELOPMENT REPORT

ISOTOPIC EQUILIBRIA OF NITROSYL CHLORIDE

by

Riley Schaeffer and Hampton Smith

June 4, 1957

Ames Laboratory
at
Iowa State College
F. H. Spedding, Director
Contract W-7405 eng 82

U N C L A S S I F I E D

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

ISC-867

This report is distributed according to the category Chemistry-General, as listed in TID-4500, February 15, 1958.

Legal Notice

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission to the extent that such employee or contractor prepares, handles or distributes, or provides access to, any information pursuant to his employment or contract with the Commission.

Printed in USA. Price 50 cents. Available from the

Office of Technical Services
U. S. Department of Commerce
Washington 25, D. C.

ISC-867

Abstract

The electrolytic solvent characteristics of liquid nitrosyl chloride and general consideration of the factors affecting suitability of a system for isotope separation suggest that exchange reactions of NOCl might provide an interesting and useful means for the separation of the stable isotopes of nitrogen or of chlorine, or of both in a simultaneous process. Vibrational frequencies of isotope substituted NOCl molecules are calculated and used to estimate equilibrium constants for exchange of nitrosyl chloride with nitric oxide and with chlorine. Provisional experimental values of the equilibrium constants are given.

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

ISC-867

Isotopic Equilibria of Nitrosyl Chloride

by

Riley Schaeffer and Hampton Smith

As a system for the separation of nitrogen or chlorine isotopes, nitrosyl chloride exchange with nitric oxide or chlorine offers many potential advantages. Since both N^{15} and Cl^{37} have unusually low thermal neutron cross sections compared to the more abundant isotopes, a separation which is in principle capable of producing either or both deserves further attention. It appeared desirable to attempt to evaluate the magnitude of separation factor to be expected, both theoretically and experimentally.

If vibrational frequencies of the various isotopic molecules are known, the method described by Urey¹ and by Bigeleisen and Mayer² may be used to calculate the desired equilibrium constants. The frequencies and partition function ratios for the $N^{14}O$ - $N^{15}O$ and Cl_2^{35} - Cl_2^{37} pairs have been calculated.¹ Although the vibrational spectrum of normal nitrosyl chloride has been observed, the vibrational frequencies for the various isotope-containing molecules have not been determined except in one instance.³ The required frequencies were consequently calculated from the force constants determined by Pulford and Walsh⁴ using the FG matrix method.⁵ The calculated frequencies for the various molecules are tabulated in Table I.

Table I
Calculated Vibrational Frequencies
of Isotope Substituted Nitrosyl Chlorides

	ω_1	ω_2	ω_3
$N^{14}OCl^{35}$	325 cm. ⁻¹	599 cm. ⁻¹	1800 cm. ⁻¹
$N^{14}OCl^{37}$	321	597	1800
$N^{15}OCl^{35}$	323	583	1767
$N^{15}OCl^{37}$	319	582	1767

In one case, that of the $N^{14}OCl^{35}$ - $N^{14}OCl^{37}$ pair, Eberhardt and Burke³ have observed a change of 4 cm.⁻¹ in the ω_1 frequency, although the frequencies calculated here are slightly lower than the observed values. Since the partition function ratios are more sensitive to $\Delta\omega$ values than to the absolute magnitude of ω (within a small range) the agreement can be considered good.

The exchange reactions considered are:

Table II presents calculated equilibrium constants for the two reactions at three temperatures.

Table II
Equilibrium Constants for Isotopic Exchange Reactions
of Nitrosyl Chloride

	K_1	K_2
25°C.	1.015	
0°C.	1.017	1.003
-25°C.	1.020	1.007

The equilibrium constants for the equilibria involving N^{14} and N^{15} are lower than the constants for reactions currently used for concentration of N^{15} (compare with 1.035 for the $NH_3-NH_4^+$ process of Urey⁶). The equilibria we are presently concerned with offer other advantages which make experimental check of the calculated constants desirable. Thus, the direct decomposition of $NOCl$ to NO and Cl_2 can probably be readily accomplished by electrolysis.⁷ The high conductivity of solutions of materials such as $FeCl_3$ in nitrosyl chloride suggests that electrolysis can be carried out with relatively low power losses, although further study of the reaction will be required. The direct combination of nitric oxide with chlorine is a simple, third order reaction and can probably be efficiently used to supply reflux at the top of an exchange column. This scheme thus avoids the production of large amounts of by-products usually associated with chemical separation procedures. (Urey's process, for example, produces large amounts of $NaNO_3$ or another salt depending on the acid and base used to provide reflux at top and bottom of the column. Similar problems arise with other reactions which have been proposed.) Furthermore, the reaction can be run in such a manner as to provide Cl_2^{37} as a by-product at no additional power cost. Although the single-stage enrichment factor is lower for the chlorine exchange, this is in large part balanced by the fact that the desired isotope makes up approximately 25% of natural chlorine. It is of interest to note that the calculations indicate that the heavier chlorine isotope will be less stable than the lighter in nitrosyl chloride, a

feature reflecting the low strength of the N-Cl compared to the Cl-Cl bond.

Experimental

Preparation of materials

Nitric oxide used in this study was obtained from the Olin Mathieson Chemical Corporation (Joliet, Ill.), and was further purified by fractional condensation techniques in a conventional vacuum system using stopcocks lubricated with a Kel-F grease. Nitrosyl chloride was prepared by the reaction of nitrogen dioxide with moist potassium chloride and purified by fractional condensation in the vacuum system.⁸

Procedure

Samples of purified nitric oxide and nitrosyl chloride were sealed from the system in glass vessels and allowed to reach isotopic equilibrium at room temperature. It should be noted that the sample size was such that in all cases a liquid phase was present although the calculations made above apply to the exchange in a homogeneous gas system. After a period of a few hours, a period which varied from sample to sample, the mixture was introduced once more into the vacuum system and the nitric oxide separated from the nitrosyl chloride by fractional condensation through a trap maintained at -157°C . which retained the nitrosyl chloride but allowed the nitric oxide to pass through to a liquid-nitrogen-cooled trap. The nitrosyl chloride was then allowed to react with mercury to liberate nitric oxide. Both samples of nitric oxide were converted to pure nitrogen by passage over a bed of copper maintained at 650°C . in a quartz tube, and the ratio of the two nitrogen isotopes was determined mass

spectrometrically.⁹ The results are recorded in Table III. The equilibrium constant for nitrogen exchange is only approximately one half of the calculated value.

Table III
Exchange of Nitric Oxide with Nitrosyl Chloride

Sample No.	$^{15}\text{N}/^{14}\text{N}$	K_1
1A*	0.003690	
1B*	0.003720	1.008
2A	0.003670	
2B	0.003675	1.0001
3A	0.003625	
3B	0.003650	1.007
4A	0.003650	
4B	0.003675	1.007

* A samples are obtained from the NO whereas B samples are obtained from the NOCl.

It was considered desirable to check directly the assumption that the decomposition potential should be zero for the electrolysis of nitrosyl chloride. A small cell containing two platinum electrodes was filled with carefully dried and purified nitrosyl chloride. Measurements of current vs. applied voltage were made using an uncalibrated voltmeter and milliammeter. The observed data are recorded in Table IV and are plotted in Fig. 1.

Table IV

Current vs. Potential Measurements for Liquid NOCl

Applied Voltage (volts)	Current (milliamperes)
5.7	1.0
5.3	0.92
4.7	0.82
4.2	0.72
4.0	0.70
3.3	0.60
2.7	0.50
2.2	0.40
1.6	0.30
1.0	0.20
0.3	0.10

It will be observed that the experimental points fall on a straight line which extrapolates to zero current at approximately -0.3 volts. The negative value for the decomposition potential may indicate a small back-potential arising from the constant presence of the products of electrolysis in the solution. However, the difference from zero is also within reasonable error for the uncalibrated voltmeter used.

Discussion

The separation factor for the fractionation of nitrogen isotopes by use of the nitrosyl chloride-nitric oxide system is relatively small.

Fig. 1 - Current vs. Applied Potential in Liquid NOCl.

However, the chemical simplicity of the system and the relatively low power consumption that should be required both suggest that a cost analysis of the system might be desirable.

References

- (1) H. C. Urey, J. Chem. Soc., 562 (1947).
- (2) J. Bigeleisen and M. Mayer, J. Chem. Phys., 15, 261 (1947).
- (3) W. H. Eberhardt and T. G. Burke, J. Chem. Phys., 20, 529 (1952).
- (4) A. G. Pulford and A. Walsh, Trans. Faraday Soc., 47, 347 (1951).
- (5) E. B. Wilson, Jr., J. C. Decius and P. C. Cross, Molecular Vibrations, McGraw-Hill Book Company, New York, N. Y., 1955.
- (6) H. G. Thode and H. C. Urey, J. Chem. Phys., 7, 34 (1939).
- (7) (a) A. B. Burg and G. W. Campbell, Jr., J. Am. Chem. Soc., 70, 1964 (1948).
(b) A. B. Burg and D. E. McKenzie, J. Am. Chem. Soc., 74, 3143 (1952).
- (8) Whittaker, Lundstrom and Merz, Ind. Eng. Chem., 23, 1410 (1931).
- (9) Mass spectrometric determinations were carried out with the cooperation of Dr. H. J. Svec. The conversion of nitric oxide to nitrogen was carried out by Mr. Gerald Brennan. We wish to express our gratitude to both individuals for their assistance.