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Reactions of Methyl with Ethyl Radicals

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The assumptions as to constancy of configuration of the ions and their vibrational frequencies with change in physical state discussed previously[1] must be kept in mind. Some of the ions for which gaseous entropies can be calculated can not exist as stable ions in aqueous solution. However, in other cases although the ions are stable, no experimental partial molal entropies are available. Consequently, it is not now possible to arrive at much in the way of generalities concerning the classes of ions represented in Table I.

[1] A. P. Altshuller, J. Chem. Phys. **24**, 642 (1956); **26**, 404 (1957).

[2] W. M. Latimer, *The Oxidation States of the Elements and their Potentials in Aqueous Solution*, (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1952), second edition.

[3] F. D. Rossini, *et al.*, Selected Values of Chemical Thermodynamic Properties, Natl. Bur. Standards Circ. 500 (1952).

Fractionation of Nitrogen and Oxygen Isotopes between Gaseous NO and Liquid NOCl

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THE differences in the bonds formed by both nitrogen and oxygen in the molecules NO and NOCl indicated the possibility for isotopic fractionation of these elements upon equilibration of NO gas with NOCl liquid. Pauling[1] points out that the odd electron molecule NO has the effective structure $:\mathrm{N}\vdots\vdots\mathrm{O}:$, while NOCl is about 50% ionic in character with an assumed resonance between the structures[2]

$$:\ddot{\mathrm{O}}::\ddot{\mathrm{N}}:\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}: \quad \text{and} \quad :\mathrm{O}\vdots\vdots\mathrm{N}:^{+}:\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}:^{-}.$$

The reversibility of the reaction, $2NO+Cl_2=2NOCl$, suggested a means by which exchange might be expected to occur.

Commercial NOCl was purified by distillation under a blanket of dry, oxygen-free helium in a vacuum jacketed 30-plate bubble cap column. The use of a lubricant in the still head was eliminated by removing product NOCl through a ball take-off valve, which was opened intermittently by a solenoid. The purification of tank NO was accomplished by a series of vaporizations and condensations on a vacuum line, discarding tops and bottoms. The two phases were contacted in a flask by vigorous stirring of the liquid at −50°C for a period of four hours. A previous experiment with NO enriched in the isotope N^{15} showed that exchange was complete within this time interval. After equilibration, samples of both phases were taken in breakseals, the NOCl was reduced quantitatively with mercury to NO,[3] and isotopic analyses of the NO were made with a mass spectrometer. The N^{14}/N^{15} ratio was determined from mass peaks 30 and 31; the O^{16}/O^{18} ratio, from mass peaks 30 and 32.

TABLE I. Single-stage fractionation factors for nitrogen and oxygen.

Exp No.	$\alpha_{N^{14}/N^{15}}$, 95% C. I.	$\alpha_{O^{16}/O^{18}}$, 95% C. I.
1	1.017 ± 0.003	—
2	1.010 ± 0.006	1.013 ± 0.006
3	1.013 ± 0.003	1.011 ± 0.002

The experimental results are given in Table I, where α, the single stage fractionation factor, is equal to the isotopic ratio in the NO phase divided by the isotopic ratio in the NOCl phase. The data show that both the N^{15} and the O^{18} tend to concentrate in the liquid NOCl.

Recently, Schaeffer[4] has calculated the vibrational frequencies of NOCl and has found isotopic shifts of 2, 16, and 33 cm^{-1} for the V_1, V_2, and V_3 frequencies, respectively. Fletcher and Begun[5] find experimentally an isotopic shift of 33 cm^{-1} in the vibrational frequency of NO. Through the use of these data with the equations of Bigeleisen and Mayer,[6] the isotopic fractionation factor for the exchange reaction $N^{14}OCl+N^{15}O=N^{15}OCl+N^{14}O$ is calculated to be 1.026 at −50°C.

It can be seen that the experimental value of $\alpha-1$ for this exchange is only about 50% of the calculated value. This was found by Schaeffer[4] to be the case at room temperature, also.

[1] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, 1940), second edition, p. 267.

[2] J. A. A. Ketelaar and K. J. Palmer, J. Am. Chem. Soc. **59**, 2629 (1937).

[3] E. W. R. Steacie and W. McF. Smith, Can. J. Research **16B**, 1 (1938).

[4] R. Schaeffer (private communication, October 17, 1957).

[5] W. H. Fletcher and G. M. Begun, J. Chem. Phys. **27**, 579 (1957).

[6] J. Bigeleisen and M. G. Mayer, J. Chem. Phys. **15**, 261 (1947).

Reactions of Methyl with Ethyl Radicals

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MIXTURES of acetone and 2,2,4,4 tetradeuteropentanone were photolyzed to prepare $CH_3CD_2CH_3$ for a standard mass spectra. Gas chromatography was used to separate and measure the products which were collected for the mass spectrometer. From the analyses one can calculate the rate ratio of the following combination reactions; (1) methyl-methyl, (2) methyl-ethyl, and (3) ethyl-ethyl;

$$\frac{R^2(\text{propane})}{R(\text{butane})\times R(\text{ethane})}=\frac{k_2{}^2}{k_3\cdot k_1}.$$

The observed ethane is corrected for the ethane formed by ethyl-ethyl disproportionation by subtracting 0.1 butane.[1] The average ratio from six runs is 4.0±0.2. This can be combined with recent measurements[2] of the rate constants of reactions 1 and 3 to get $k_2=4.2\pm 0.5\times 10^{13}$ cc mole^{-1} sec^{-1} at 100°. This is larger than the other rate constants which are $k_1=2.2\times 10^{13}$ and $k_3=2.0\times 10^{13}$.

The methyl-ethyl collision can also produce CH_4 and $CH_2=CD_2$ by a disproportionation type reaction. The observed ethylene minus 0.1 butane should equal the observed methane minus that formed by abstraction. As the temperature and pressure are decreased below 100° and 60 mm the abstraction decreases as shown by the decrease of CH_3D. At 90° and 20 mm the observed ethylene minus 0.1 butane equals the methane within measurement error. The ratio disproportionation/combination is given by methane/propane which is 0.06±0.01. This can be compared to 0.1 for ethyl-ethyl and 0.63 for isopropyl-isopropyl.[3]

All runs were kept under 1% decomposition.

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[1] Kutschke, Wijnen, and Steacie, J. Am. Chem. Soc. **74**, 714 (1952).

[2] A. Shepp and K. O. Kutschke, J. Chem. Phys. **26**, 1020–28 (1957).

[3] C. A. Heller and Alvin S. Gordon, J. Phys. Chem. **60**, 1315 (1956).

Negative Ion Formation in N_2O and in NO by Electron Impact†

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AS part of a study of the radiation chemistry of nitrous oxide, a mass spectrometric investigation was made of the negative ions formed in N_2O on electron impact. Electrons with energies from 0 to 50 ev were used.

Only the O^- ion was found. Its ion efficiency curve was obtained. The energy scale was established by using the low energy resonance capture peak of Cl^- from HCl. This reference point has been accurately determined by Fox to be 0.65 ev.[1]

A low energy resonance capture peak was observed for O^- at 2.5±0.2 ev. The ion efficiency curve then dropped to a minimum at about 5 ev (the intensity here was 15% of its value at the peak). There was a slow rise to an irregular plateau which extended from 15 to 50 ev. The intensity in this range was about 40% of that of the low-energy peak.

The resonance capture is presumably produced by the reaction

$$N_2O(^1\Sigma)+e\rightarrow N_2(^1\Sigma)+O^-(^2P).$$

The exact mechanism for the formation of O^- at higher energies can not be known with certainty. It could be due in part to any of the following: low-energy secondary electrons ejected from electrode surfaces by the primary beam, the productions of O^- accompanied by nitrogen in an excited state or as the ion, N_2^+.

NO^- was not found. In addition the negative ion spectrum was obtained for nitric oxide using electrons from 0 to 50 ev, and the only ion found was O^-. Apparently NO^- can not be formed by electron collision in NO or N_2O at low pressure. If negative ions other than O^- are present in N_2O or NO, it will probably be at higher pressure where dimerization of NO is possible.

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[1] R. E. Fox, J. Chem. Phys. **26**, 1281 (1957).

Hydrogen Formation in Concentrated Aqueous Sodium Sulfate Solutions by Cobalt-60 Gamma-Ray Radiation

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THE effect of ionizing radiation on water has been interpreted by assuming an initial decomposition of water into H atoms and OH radicals. The interaction of the H atoms and OH radicals with themselves as they diffuse away from their site of origin into the bulk of the solution gives rise to the molecular products H_2 and H_2O_2. In solution, interaction of these radicals or molecular products with the solute may occur. The effect of the interaction may manifest itself by altering the molecular yields.[1-7]

The gamma radiation was provided by a 900-curie cobalt-60 source.[8] The rate of energy absorption was calibrated with the Fricke dosimeter assuming the value 15.6 ferrous molecules oxidized per 100 ev of absorbed energy.[9] Determinations of ferric ion were made on a Cary recording spectrophotometer at 3050 A and calculated using a molar extinction coefficient of 2240 at 25°C.[9] The *p*H measurements were made with a Beckman *p*H meter standardized with Cenco standard buffer solutions. All chemicals were Baker and Adamson reagent grade and were used without further purification. Water from a Barnstead still was purified[10] and stored in silica vessels.

The Na_2SO_4 solutions, containing $10^{-3}M$ KBr to protect the molecular hydrogen formed from radical attack,[11] were degassed by alternately freezing, evacuating to 10^{-6} mm pressure and thawing. The S.T.P. hydrogen volumes were determined by ignition with oxygen on a platinum filament. The method utilized by Mahlman and Schweitzer[12] was used to calculate the energy absorption of the solutions. This method