Nitrogen Pentoxide Formation in the OxygenNitric Oxide Reaction

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Sulfide in Zinc-Oxide Luminophors

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March 30, 1950

THE green luminescence emission observed in luminophors made by firing zinc oxide in hydrogen,[1] consisting of a characteristic broad band,[2] has been attributed to the presence of "excess" or "free" zinc[3] as an activator.

Two facts leave little doubt that the presence of a small amount of sulfide (zinc sulfide in solid solution), rather than free zinc, is necessary to obtain the observed green emission: (1) Reagent grades of zinc oxide contain approximately 0.01 percent zinc sulfate, which is reduced to zinc sulfide during the hydrogen-firing. The sulfide can be detected (by the plumbite-paper test) in the luminescent product. (2) Without the use of hydrogen or other reducing agent (to produce the postulated free zinc), zinc-oxide luminophors having this same green emission can be produced by mixing with zinc oxide a small amount of sulfide-introducing agent, such as zinc sulfide, sulfur, sodium thiosulfate or ammonium sulfide, and firing the mixture in a vessel with a close-fitting cover.

Further support is given by the fact that the substitution of zinc selenide for the small addition of zinc sulfide gives a zinc-oxide luminophor with an orange emission.

[1] E. Beutel and A. Kutzelnigg, Monatshefte f. Chemie **61**, 437 (1932).
[2] R. E. Shrader and H. W. Leverenz, J. Opt. Soc. Am. **37**, 939 (1947).
[3] A. Schleede, Angew. Chemie **50**, 1908 (1937).

Nitrogen Pentoxide Formation in the Oxygen-Nitric Oxide Reaction

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March 31, 1950

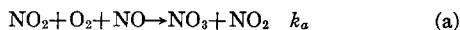THE standard free energy change of the reaction

$$2NO + \tfrac{3}{2}O_2 \rightarrow N_2O_5 \tag{I}$$

may be found from the well-known thermodynamic properties of NO and O_2, together with the heat of formation[1] of N_2O_5, and a reasonable estimate of the standard entropy of the latter as close to that of N_2O_4. This calculation indicates that at room temperature and partial pressures of the order of a few hundred millimeters of mercury the above reaction should proceed practically to completion. Extension of previous kinetic considerations[1-3] leads to the expectation that under proper conditions the rate of the above process may be such as to cause significant competition with the reaction

$$2NO + O_2 \rightarrow 2NO_2 \tag{II}$$

hitherto considered the sole process in this reacting system.

The proposed mechanism for reaction (I) is as follows:

$$NO_2 + O_2 + NO \rightarrow NO_3 + NO_2 \quad k_a \tag{a}$$
$$NO_3 + NO_2 \rightarrow N_2O_5 \quad k_b \tag{b}$$
$$NO_3 + NO \rightarrow 2NO_2 \quad k_c. \tag{c}$$

Step (a) is seen to be the reverse of step (3) in the mechanism of nitrogen pentoxide decomposition,[1,2] whereas steps (b) and (c) are identical respectively with (2) and (4) of that mechanism. By familiar steady-state considerations the resulting rate expression is

$$\frac{d(N_2O_5)}{dt} = \frac{k_a(NO_2)(O_2)(NO)}{1 + k_c(NO)/k_b(NO_2)}.$$

Comparison of this with the well-known termolecular rate expression for reaction (II) indicates that the conditions favorable to occurrence of reaction (I) involve a small concentration of NO

and a large concentration of NO_2. A further point of importance concerns the quasi-bimolecular character[2] of step (b). In order to make the effective value of k_b as great as possible, the concentration of molecules effective for collisional deactivation should be large—it is desirable to add a chemically indifferent foreign gas in large quantity.

Experimental verification of the above predictions regarding formation of nitrogen pentoxide has been obtained, the characteristic infra-red absorption spectrum[3] being used for detection and quantitative estimation. The spectrometer and cells were the same as previously described.[3] Both the strong band at about 1350 cm^{-1} and a weaker one at about 860 cm^{-1} were used. The latter is completely resolved from bands of NO_2 and N_2O_4, even at the highest concentrations of the latter substances. The former is partially obscured by a neighboring N_2O_4 band, but use of a compensating cell filled with the proper amount of N_2O_4 and placed in the other beam of the spectrometer satisfactorily eliminates this interference. (A similar procedure was used to eliminate partial obscuring of the 860 cm^{-1} band by overlapping bands of SF_6.) The absorption cell was filled at room temperature with a mixture (in measured amounts) of NO, NO_2—N_2O_4 and either CO_2 or SF_6. A large reservoir space adjacent to the cell was then filled with pure oxygen at atmospheric pressure. By opening a large bore stopcock, oxygen was admitted as rapidly as possible to the gas mixture, the initial pressure being chosen so that oxygen was finally present in considerable stoichiometric excess. The chemical changes were completed in a few seconds. After closing the stopcock the infra-red spectrum was traced.

These studies have shown unequivocally that N_2O_5 is formed in significant amounts. In a typical case, the initial partial pressure of NO was 100 mm Hg, while those of N_2O_4 and SF_6, respectively, were some 100 mm and 300 mm Hg. After admission of oxygen to a total of one atmosphere pressure, the partial pressure of N_2O_5 proved to be some 10 mm Hg—a yield of 20 percent. Variation of yields with initial NO_2 concentration followed the general course predicted by the above rate expression. For otherwise constant conditions, the efficacy of added gases in promoting N_2O_5 formation increased sharply in the order O_2, CO_2, SF_6—the last being especially effective. This variation is excellent evidence for the quasi-bimolecular character of step (b). The high efficiency of SF_6 is expected in view of the large number of internal degrees of freedom available for collisional deactivation. Analysis of the yield data so far obtained indicate that the termolecular rate constant for step (a) cannot differ greatly in magnitude from that for the well-known reaction (II)—this comparison applying at some 300° Kelvin. The previous considerations[1] suggest that k_a has a nearly negligible temperature coefficient.

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[3] R. A. Ogg, Jr., W. S. Richardson, and M. K. Wilson, J. Chem. Phys. **18**, 573 (1950).

Influence of Molecular Structure of Ethylene Chloride on Ion-Association of Dissolved Salts

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March 31, 1950

BJERRUM[1] has derived an equation relating the thermodynamic dissociation constant, K, of an electrolyte to the temperature, the dielectric constant, D, of the solvent and the contact distance, a, of the two oppositely charged ions. A simple model is assumed in which the only force of interaction between

TABLE I.

Salt	$K \times 10^5$ at 25°C In ethylene chloride	In ethylidene chloride
o-chloro	a 3.92 ±0.12	0.414 ±0.010
o-methoxy	7.85 ±0.25	1.12 ±0.020
m-methoxy	3.89 ±0.12	0.415 ±0.010

a Recalculated from data of Ramsey and Colichman by use of method of least squares to establish more precisely the linear relation between the functions involved.

the ions is Coulombic and the ions are considered to be rigid unpolarizable spheres in a continuous medium of uniform dielectric constant equal to the macroscopic dielectric constant of the pure solvent. For a uni-univalent electrolyte, this equation takes the form

$$K^{-1} = \frac{4\pi N}{1000}\left(\frac{\epsilon^2}{DkT}\right)^3 Q(b),$$

in which

$$b = \frac{\epsilon^2}{aDkT} \quad \text{and} \quad Q(b) = \int_2^b e^y y^{-4} dy$$

where $y = \epsilon^2/(rDkT)$. Other symbols have their usual meaning.

That deviations from this equation will occur for systems which differ appreciably from the idealized model is expected. An apparent deviation has been reported by Ramsey and Colichman.[2] They found the dissociation constant at 25°C of o-chlorophenyltrimethylammonium perchlorate in ethylene chloride (1,2-dichloroethane) to be approximately tenfold greater than in ethylidene chloride (1,1-dichloroethane). Since the dielectric constants of these solvents at 25°C are approximately equal, 10.23 for ethylene chloride and 10.00[3] for ethylidene chloride, and since there is no apparent reason why the a-values of this salt should be appreciably different in these two very similar solvents, this large difference in K-values seems anomalous. The fact that the product, $\Lambda_0\eta$, of this salt has the same value within experimental error in these two solvents lends support to the conclusion that its a-values should be substantially the same.

In order to establish with certainty that a large difference in the K-values of a given salt in these two solvents exists, the K-value of the ortho-chloro salt in ethylidene chloride and those of the ortho-methoxy and meta-methoxy salts in ethylene chloride have been redetermined. In addition the K-values of the two methoxy salts were determined in ethylidene chloride. Shedlovsky's[4] modification of the Fuoss and Kraus[5] conductance equation was used in obtaining these K-values, given in Table I.

Since the K-values of each of these three salts is very much (from seven to ten times) larger in ethylene chloride than in ethylidene chloride, it seems probable that these differences should be attributable to certain fundamental differences in these two solvents which are not apparent from their macroscopic properties.

On the basis of the reasonable assumption that the a-value of each of the salts is the same in these solvents it follows from the above equation that the large difference in K-values may be due to a difference between the macroscopic dielectric constant of at least one of the solvents and its effective dielectric constant, that is, the dielectric constant which is effective in determining the stability of the associated ion-pair of an electrolyte in that solvent. The conclusion that such a difference does not exist in ethylidene chloride solution is justified by the fact that the molecules of this solvent are known to exist in but one form. However, the results of a number of investigations have established the existence of restricted rotation about the carbon-carbon bond in the molecules of ethylene chloride which consists of three potential minima, 120° apart, in one complete rotation about this bond axis. From a study of the relative intensities of certain Raman lines in the vapor and liquid phases of ethylene chloride, Mizushima et al.,[6] have estimated the equilibrium ratio of the number of molecules in the gauche forms (an angle of 60° between the C—Cl bonds viewed along the C—C bond axis) to the number in the trans-form (180°

between the C—Cl bonds) to be 1.3:1 in liquid ethylene chloride at 25°C. They have also calculated the dipole moment of the gauche forms (one the mirror image of the other) to be 2.55×10^{-18} e.s.u. For comparison the dipole moment of ethylidene chloride molecules, determined by Ghosh et al.,[7] is 2.045×10^{-18} e.s.u.

The existence of these two isomers of ethylene chloride, the polar (the two gauche forms) and the non-polar (trans-) form leads to the conclusion that an ion in ethylene chloride will attract preferentially the gauche molecules and thereby produce an enhancement of the relative population of this form (N_g/N_t) in the near vicinity of the ion above the average in the pure solvent. This long-range ion-dipole interaction would make the effective dielectric constant in ethylene chloride greater than the macroscopic dielectric constant of this solvent and thus cause the measured K-value to be greater than that calculated by the above equation by use of the macroscopic dielectric constant and the correct a-value.

An independent method of determining the correct value of the parameter a to be used in the above equation is not in general available. However, the assumption that the a-value of a salt in ethylene chloride is the same as it is in ethylidene chloride provides, in this case, an independently determined a-value to be used for a given salt in ethylene chloride. The a-value found for each of the salts (in the order given in Table I) in ethylidene chloride are 3.50×10^{-8} cm, 3.85×10^{-8} cm and 3.50×10^{-8} cm, respectively. On substitution of the a-value, thus obtained, and the corresponding K-value, determined in ethylene chloride, the effective dielectric constant of ethylene chloride, consistent with these values, is evaluated by successive approximations. The average of the two values of the effective dielectric constant thus obtained is 11.9±0.1. The K-values of these three salts in ethylene chloride calculated by use of 11.9 for D are 3.82×10^{-5}, 8.18×10^{-5}, and 3.82×10^{-5}, respectively. These values are seen to agree within experimental error with those measured.

That the effective dielectric constant of ethylene chloride in the near vicinity of an ion may be as much as 1.7 units greater than its macroscopic dielectric constant (10.23) is indicated by the crude value of 15.5 (calculated) for the dielectric constant of the pure liquid gauche form by Onsager's equation, approximating its density and refractive index to be those of ethylene chloride.

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[4] T. Shedlovsky, J. Frank. Inst. 225, 739 (1938).
[5] R. M. Fuoss and C. A. Kraus, J. Am. Chem. Soc. 55, 476 (1933); R. M. Fuoss, ibid. 57, 488 (1935).
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Calculation of the Heats of Formation of Alkali Halide Solid Solutions from Hildebrand's Equation

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March 27, 1950

HILDEBRAND[1] has derived the expression

$$\Delta H_f = \left(\frac{N_1 V_1 N_2 V_2}{N_1 V_1 + N_2 V_2}\right)\left[\left(\frac{\Delta E_1}{V_1}\right)^{\frac{1}{2}} - \left(\frac{\Delta E_2}{V_2}\right)^{\frac{1}{2}}\right]^2 \quad (1)$$

for the change in heat content on forming one mole of a solution from the pure liquids. ΔE, V, and N are the heat of vaporization, the molar volume and mole fraction, respectively, of the component liquids. In deriving the above equation the important