

Proton Transfer in the Radiation Chemistry of Gaseous Ammonia

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TABLE I. T is expressed in degrees Kelvin, v_1 in meters/sec and κ_S in 10^{-10} cm²/dyne.

T	v_1 (calc)	v_1 (exp)	κ_S (calc)	κ_S (exp)
10	1607	1510	0.43	0.42
30	1615	1485	0.45	0.44
60	1613	1420	0.52	0.49
80	1575	1320	0.65	0.59

Table I and are to be compared with the adiabatic compressibility calculated from Henkel's equation of state (for the density ρ and expansivity α), specific heat (c_p) and bulk modulus ($K=1/\kappa_T$), using the relation $\kappa_S=\kappa_T-\alpha^2T/\rho c_p$. The two compressibilities agree within the experimental error of about 10% at all temperatures.

Finally, the equation of state, based on a density of 1.68 g/cm³ at 0°K, may be used to obtain the density of the solid argon at its triple point, 84°K. The calculated value is 1.56 g/cm³, which may be compared with the experimental value of 1.62 g/cm³, obtained by Clusius and Weigand⁴ from the density of liquid argon and its expansion on melting. This shows that the theoretical expansion of solid argon from 0°K to 84°K is about twice that found experimentally.

Evidently the equation of state derived by Henkel yields accurate values for the specific heat and the compressibility, but does not fit the existing data for the variation with temperature of the density and longitudinal velocity of sound. A recent experiment by Guptill, Hoyt, and Robinson⁵ has confirmed our temperature variation of the longitudinal velocity. We are at present checking the density data, but it seems unlikely that a theory based on a two-constant interatomic potential can be expected to agree in detail with all the experimental data, even when anharmonic vibrations have been considered.

¹ J. H. Henkel, *J. Chem. Phys.* **23**, 681 (1955).

² Barker, Dobbs, and Jones, *Phil. Mag.* **44**, 1182 (1953).

³ J. R. Barker and E. R. Dobbs, *Phil. Mag.* **46**, 1069 (1955).

⁴ K. Clusius and K. Weigand, *Z. physik. Chem.* **B46**, 1 (1940).

⁵ Guptill, Hoyt, and Robinson, *Can. J. Phys.* **33**, 397 (1955).

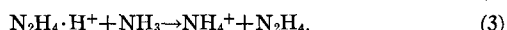
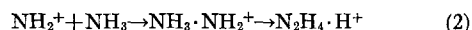
Proton Transfer in the Radiation Chemistry of Gaseous Ammonia

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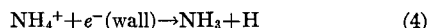
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(Received December 12, 1955)

IN our most recent paper on the alpha radiolysis of gaseous ammonia,¹ evidence was given to show that at low intensity and at pressures of several hundred millimeters, there was no measurable decomposition initiated by the recombination of ions. Furthermore, our results at that time could be explained assuming that NH_3^+ and NH_2^+ did not undergo reaction before neutralization at the wall.

In view of work now in progress, this earlier notion must be revised. The results can best be explained if the NH_3^+ and the NH_2^+ known to exist in irradiated NH_3 react with NH_3 in the gas phase by proton transfer to form NH_4^+ as follows:



The NH_4^+ may react at the wall:



Such a scheme satisfactorily accounts for the observations currently being made of the effects of pressure and intensity on the net ion yield.

Proton transfer in H_2 has been known for some time and has been reviewed by Hirschfelder, Curtiss, and Bird.² Stevenson³ has recently shown experimentally that CD_3^+ and D_3^+ are formed by such processes.

The first suggestion of the existence of NH_4^+ in the gas phase was made by J. Bartlett, Jr.,⁴ in 2-mass spectrographic study of ammonia. He reported a fragment of mass 18, but he felt that it might have been H_2O^+ .

To our knowledge, the mass spectrum of NH_3 at pressures high enough to permit molecular collisions has not been obtained. It should however show the presence of NH_4^+ and N_2H_5^+ .

¹ B. P. Burtt and T. Baurer, *J. Chem. Phys.* **23**, 466 (1955).

² Hirschfelder, Curtiss, and Bird, *Molecular Theory of Gases and Liquids* (John Wiley and Sons, Inc., New York, 1954), p. 1095.

³ D. P. Stevenson and D. O. Schissler, *J. Chem. Phys.* **23**, 1353 (1955).

⁴ J. Bartlett, Jr., *Phys. Rev.* **33**, 169 (1929).

Zinc and Cadmium Chloride Complexes in Molten Salts

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(Received November 17, 1955)

BESIDES tetrahedral ZnCl_4^{2-} , plane XCl_3^- ions ($\text{X}=\text{Zn}$ or Cd) were recently reported to form in molten XCl_2-KCl mixtures.¹ While XCl_4^{2-} is plausible, the stability of ZnCl_3^- and CdCl_3^- is open to doubt: The field of the relatively large central Zn^{2+} , or Cd^{2+} , of moderate polarizability and polarizing power, is not likely to be screened sufficiently by three coplanar Cl^- ions to prevent the formation of XCl_4^{2-} . Indeed, the experimental data support the assumption of XCl_4^{2-} instead of XCl_3^- ions. In Fig. 1 of the work quoted,¹ the Raman line ν_1 in both $\text{ZnCl}_2 \cdot \text{KCl}$ and $\text{CdCl}_2 \cdot \text{KCl}$, assigned by Bues¹ to XCl_3^- , is much less well resolved from the Hg e line than the corresponding ZnCl_4^{2-} line in $\text{ZnCl}_2 \cdot 2\text{KCl}$. This suggests that the broad Raman bands of ZnCl_2 (at 233 cm⁻¹) and CdCl_2 (212 cm⁻¹) actually did not disappear in the spectra of $\text{XCl}_2 \cdot \text{KCl}$, but that these are superpositions of the spectra of molten XCl_2 and $\text{XCl}_2 \cdot 2\text{KCl}$, i.e., of $(\text{XCl}_2)_n$ aggregates and XCl_4^{2-} ions. The small apparent shifts in the ν_1 frequency for XCl_4^{2-} , from 292 ± 3 cm⁻¹ in molten $\text{ZnCl}_2 \cdot 2\text{KCl}$ to 280 ± 3 cm⁻¹ in $\text{ZnCl}_2 \cdot \text{KCl}$ ($=\text{K}_2\text{ZnCl}_4 + \text{ZnCl}_2$), and from 243 for CdCl_4^{2-} in aqueous solution to 259 in molten KCl may also be explained by this superposition, if not by the drastic changes in the surrounding media.

A curve correlating force constants with "bond order" need not be a straight line (Bues, Fig. 3). Rather, S-shaped, it must approach the abscissa asymptotically at the origin (Fig. 1). Missing the—false—points for XCl_3^- , it passes through the points for crystalline XCl_2 , which are far distant from the straight line,

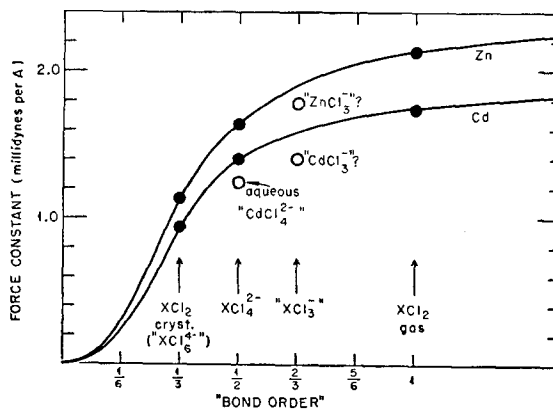


FIG. 1.

at "bond order" 0.33 corresponding to the XCl_3 coordinations of these crystals.

Very recently freezing point depression measurements² yielded the number of ions produced when CdCl_2 , ZnCl_2 , etc. are dissolved at low concentration in molten NaNO_3 both with and without added chlorides such as KCl and CaCl_2 . It was proved that CdCl_2 and ZnCl_2 associate with Cl^- to form complex anions which contain at least four chlorines. Equilibrium constants calculated from these data were consistent with presence of Cd^{2+} , CdCl_2 , and CdCl_4^{2-} , but no agreement was found on the assumption of CdCl^+ , and CdCl_3^- . Therefore, it was concluded that CdCl_3^- is an unimportant species while CdCl_4^{2-} is quite important.

Electrical conductivity, surface tension, and viscosity measurements³ have recently suggested the occurrence of complexes such as CdCl_3^- and PbCl_3^- in salt melts. The substitution of CdCl_4^{2-} ions for CdCl_3^- ions is just as feasible in the interpretation of these results as of the Raman spectra above. PbCl_3^- , however, is distinguished from CdCl_3^- and ZnCl_3^- by the lone $6s^2$ electrons of Pb^{2+} , which makes a nonplanar PbCl_3^- , with the electron pair occupying one corner of a distorted tetrahedral configuration, more plausible than PbCl_4^{2-} .

The increase in force constants from Cd to Hg chloride complexes that remained unexplained¹ may be readily understood if it is realized that the "covalent bond character" of the $\text{X}-\text{Cl}$ binding ($\text{X}=\text{Zn}, \text{Cd}, \text{or Hg}$), or, rather, the degree of mutual polarization of cation and anion, clearly is at a minimum in the cadmium compounds: Zn^{2+} , because of its smaller size, is more strongly polarizing, and Hg^{2+} is more polarizable than Cd^{2+} .

¹ W. Bues, *Z. anorg. u. allgem. Chem.* **279**, 104-114 (1955).

² E. R. Van Artsdalen, *J. Phys. Chem.* (to be published); Paper presented at Ion Pair Symposium, American Chemical Society Meeting, Minneapolis, 1955.

³ Harrap, Boardman, Palmer, and Heymann, *Trans. Faraday Soc.* **51**, 259, 268, and 277 (1955).

Electron Spin Resonance of 1,4-Naphthosemiquinone Ion*

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(Received November 14, 1955)

A PREVIOUS communication¹ pointed out that one observes the expected number ($2nI+1$) of hyperfine splitting components in the electron spin resonance (ESR) spectrum of the semiquinone ions derived from 1,4-benzoquinone and its chlorine-substituted derivatives. Here n represents the number of ring protons, and $I (= \frac{1}{2})$ is their nuclear spin. The magnetic moment of the chlorine nucleus is too small to give observable splitting. For the semiquinones from phenylquinone, 2,5 and 2,6-diphenylquinone one observes, respectively, four, three, and three components, indicating that the interaction of the unpaired electron with the protons of the substituting phenyl groups is far smaller than for those of the principal ring. We attribute this to the noncoplanar orientation of the substituting rings with the principal one.

In the naphthoquinones one is assured of coplanarity of the quinoid ring and the adjacent one, and hence one might hope for an extra ESR multiplicity. This is indeed observed for 1,4-naphthosemiquinone ion in basic alcohol solution, as shown in Fig. 1. Ignoring the protons in the 5, 6, 7, and 8 positions, one would expect three components from the hyperfine interaction of the unpaired electron with the protons in the 2 and 3 positions. One does indeed observe three groups of lines spaced 3 gauss apart. Considering that the other protons might interact much more weakly with the electron, their effect would be further to split the hyperfine levels arising from protons 2 and 3. If the protons 5 to 8 interact equally with the unpaired electron, one would expect that each level would give rise to a quintet from this ultra-hyperfine interaction. This expectation corresponds with observation, these components being separated by 0.3 gauss. This system

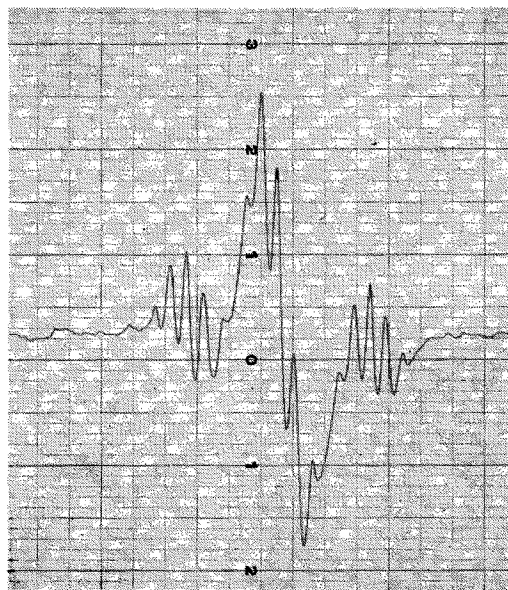


FIG. 1. The ESR absorption derivative curve for the 1,4-naphthosemiquinone ion.

is thus ideal for evaluating the relative densities of the wave function of the unpaired electron at the protons in the two rings.

The 2,3-dimethylsemiquinone ion by analogy would be expected to give seven components from the six equivalent methyl protons, and each of these should be a quintet. Seven groups are indeed observed. For the resolution at which we worked, there was an accidental coincidence of the outermost ultrahyperfine components of adjacent quintets. Since the two outermost groups are very weak, we counted the number of lines for the five inner groups and observed the expected twenty-one individual lines. These are separated by 0.57 ± 0.04 gauss.

The 2-methyl-1,4-naphthosemiquinone ion gives five groups of lines with twenty-four discernible components. The line assignment for this and numerous other naphthosemiquinone radicals is under study.

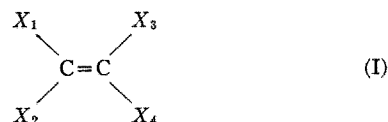
* This research was made possible by grants-in-aid from the Graduate School of the University for the purchase of equipment, and was supported in part by the U. S. Air Force under Contract AF 18 (600)-479, monitored by the Office of Scientific Research, Air Research and Development Command.

¹ John E. Wertz and Juana L. Vivo, *J. Chem. Phys.* **23**, 2441 (1955).

Nuclear Spin Coupling Constants in Halogenated Olefins

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(Received December 5, 1955)

WE give here a preliminary report of the results of a study of nuclear spin-spin couplings in a number of liquid halogenated olefins. Spectra were obtained with a Varian Associates V-4300 High Resolution NMR Spectrometer operated at 40 Mc/sec with magnetic fields of 9396 and 9983 gauss, respectively, for the H^1 and F^{19} resonances. The olefins can be represented by the general formula,



where the various X_i in (I) are listed in Table I for each compound.