

Competitive Reactions of Cl³⁸.—A model for the behavior of competitive systems has been suggested to explain the reactions of Cl³⁸ from Cl³⁷ (n, γ) reactions in CCl₄-SiCl₄, CCl₄-cyclohexane and CCl₄-benzene systems.¹⁵ The yield of CCl₃Cl³⁸ from the former was quite consistent with simple predictions of linearity with mole fraction. However, the yields of C₆H₁₁Cl³⁸ and C₆H₅Cl³⁸ from the other two mixtures were essentially independent of mole fraction, while CCl₃Cl³⁸ rose non-linearly with concentration. These yields for chlorine reactions in hydrocarbons were explained on the basis of the primary formation of an energetic complex

(15) J. M. Miller and R. W. Dodson, *J. Chem. Phys.*, **18**, 865 (1950).

of Cl³⁸ with the hydrocarbon for all Cl³⁸ atoms, with several competing modes of decomposition. From one of these, the Cl³⁸ emerged degraded in energy and reacted with CCl₄ to form CCl₃Cl³⁸ by atomic exchange while still above thermal energies. No such specificity in high energy interactions has yet been observed in tritium reactions. Both the geometry and the energetics of chlorine atom reactions are sufficiently unlike those of hydrogen atoms to account for such variations, but closely comparable experiments with halogens and tritium should prove very useful in elaborating on the simple model used in this paper.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA, PHILADELPHIA 4, PENNSYLVANIA]

Solvent Isotope Effects in H₂O¹⁶ and H₂O¹⁸

BY EDWARD R. THORNTON

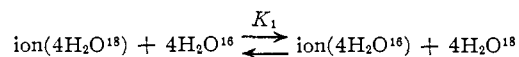
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Calculated equilibrium O¹⁸ isotope effects involving water, hydronium ion and hydroxide ion as well as some singly-charged monatomic ions are presented. It is now possible to make rate measurements in pure H₂O¹⁸. The solvent isotope effects should be considered in addition to possible primary O¹⁸ isotope effects.

Water containing 97% O¹⁸ is now available,¹ so it will be possible to measure rates in this solvent in the near future. Therefore, it is interesting to note some expected solvent isotope effects for equilibria involving transfer of ions between H₂O¹⁶ and H₂O¹⁸. These effects should be taken into account in addition to primary isotope effects when kinetic isotope effects in the two waters are analyzed.

The calculations were performed using the vibrational transitions previously recorded for H₂O¹⁶ species.² The shifts for the O¹⁸ species were calculated using theoretical formulae for the normal vibrational frequencies based on a harmonic oscillator approximation. Although this approximation neglects anharmonicities, the errors in the isotope effects should be quite small because the difference in anharmonicity between O¹⁶ and O¹⁸ species should be very small.

Singly-charged Monatomic Ions.—The librational frequencies of the four water molecules which surround a singly-charged monatomic ion are different from the librational frequencies of water molecules in pure water, and this difference gives rise to an isotope effect. The equilibrium constants for the reaction



have been calculated using the method employed by Bader² for H₂O vs. D₂O. Bader's observed librational frequencies were used for H₂O¹⁶, and the shifts were calculated from the fact that they should be related inversely to the square root of the average moment of inertia of the molecules. The moments of inertia were calculated by as-

suming the H-O bond length to be 0.96 Å,³ and the HOH angle to be 105°,⁴ using the formula in Herzberg's book.⁵ The resulting frequencies are listed in Table I, together with the equilibrium constants K_1 . One exception which should be noted is that I⁻ was assumed to be 6-coordinated,² not 4-coordinated.

TABLE I

CALCULATED LIBRATIONAL FREQUENCIES AND EQUILIBRIUM CONSTANTS FOR TRANSFER OF IONS BETWEEN H₂O¹⁸ AND H₂O¹⁶ AT 25°

Ion	Librational frequencies, cm. ⁻¹		K_1
	H ₂ O ^{16a}	H ₂ O ¹⁸	
(H ₂ O)	667	665.12
F ⁻	698	696.04	0.99818
Cl ⁻	598	596.32	1.00448
Br ⁻	573	571.39	1.00611
I ^{-b}	587	585.35	1.00782
Li ⁺	664	662.13	1.00020
Na ⁺	635	633.21	1.00208
K ⁺	625	623.24	1.00273
Rb ⁺	618	616.26	1.00318
Cs ⁺	613	611.28	1.00351

^a Ref. 2. ^b 6-Coordinated, not 4-coordinated.

Water, Hydronium and Hydroxide Ions.—For equilibria among water, hydronium and hydroxide ions, it was necessary to take account of the internal vibrations and the translations as well as the librations. Calculations of the partition function ratios Q'/Q , where the prime refers to the O¹⁸ species, for H₂O, H₃O⁺ and HO⁻ were performed, using the same frequencies and technique employed by Bader.² The frequencies of the O¹⁸ species were calculated from the O¹⁶ frequencies using the

(3) L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, p. 226.

(4) G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., Princeton, N. J., 1945, p. 170.

(5) Ref. 4, pp. 509 f. The principal axes were chosen by inspection.

(1) YEDA Research and Development Co. Ltd., Weizmann Institute of Science, Rehovoth, Israel.

(2) R. F. W. Bader, Ph.D. Thesis in Organic Chemistry, M.I.T., 1957; C. G. Swain and R. F. W. Bader, *Tetrahedron*, **10**, 182 (1960).

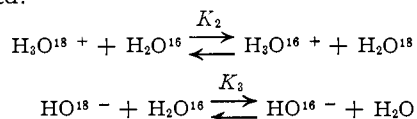
formulas in Herzberg's book⁶ for H₂O and H₃O⁺ together with the familiar formulae for diatomic molecules for HO⁻. The bond length and angle of H₂O were as above. The bond length and angle of H₃O⁺ were taken to be 0.98 Å.⁷ and 107°.⁸ The bond length of HO⁻ was of course not needed. The librational frequency shifts were calculated from the inverse square roots of the average moments of inertia,² calculated according to Herzberg's formula.⁵ The calculated frequencies for O¹⁸ species and resulting partition function ratios are in Table II.

TABLE II
FREQUENCIES OF H₂O, H₃O⁺ AND HO⁻ AND ISOTOPIC PARTITION FUNCTION RATIOS AT 25°

Molecule	Frequencies, cm. ⁻¹		Degen- eracy	Q'/Q
	O ^{16a}	O ¹⁸		
H ₂ O	3440	3431.11	1	1.2752
	1645	1638.95	1	
	3440	3425.90	1	
	667	665.12	3	
H ₃ O ⁺	3235	3230.22	1	1.3047
	1150	1141.46	1	
	2590	2578.27	2	
	1700	1695.80	2	
	643	642.18	3	
HO ⁻	3615	3603.05	1	1.2279
	477	475.42	2	

^a Ref. 2.

From these partition function ratios two especially interesting equilibrium constants can be calculated.



It is found that $K_2 = 1.2752/1.3047 = 0.9774$ and $K_3 = 1.2752/1.2279 = 1.0385$.

Discussion

The temperature dependence of these equilibrium isotope effects could be calculated, but since isotope

(6) Ref. 4, pp. 187, 188, respectively.

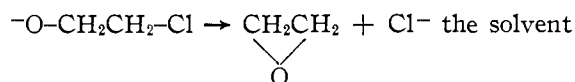
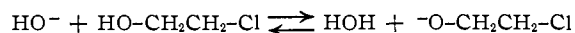
(7) C. C. Ferriso and D. F. Hornig, *J. Chem. Phys.*, **23**, 1464 (1955).

(8) Taken as a compromise between 105° for water⁴ and 109° (tetrahedral), this angle is also the observed one in NH₃ (ref. 4, p. 439).

effects are usually not very temperature dependent, this has not been done.

The effects of the halide ions, although fairly small, should be considered when studying reactions involving the production or destruction of these ions. Fluoride has $K_1 < 1$ because it increases the structure of water, while all the other ions break down the structure of water.

The isotope effects for the hydronium and hydroxide ions show that H₃O¹⁶ + is a stronger acid than H₃O¹⁸ +, and that HO¹⁸ - is a stronger base than HO¹⁶ -. In many reactions involving H₂O, H₃O⁺ and HO⁻ (or the analogs HO-C≡ and H₂O⁺-C≡) a bond to oxygen is being made or broken in the transition state, and a primary isotope effect due to that bond will appear along with the solvent isotope effect. However, in reactions involving a prior equilibrium, e.g.



isotope effect alone will determine the relative rates in H₂O¹⁶ and H₂O¹⁸.

The isotope effect K_2 for changing O<(neutral) to +O<(positively charged) means that positive charge formation is more favorable on the heavy than on the light oxygen atom. A reaction such as enolization by water as the base, in which positive charge is developed on the oxygen atom in the transition state, might therefore have an *inverse* kinetic isotope effect. This tendency for the heavy water to react faster would be lessened by the primary isotope effect and might be overbalanced by a large primary effect to give a "normal" kinetic isotope effect. It is possible, however, that some significant results could be obtained by considering these two opposing effects.

Reactions similar to K_3 , *i.e.*, in which a bond is formed to a hydroxide ion, may in some cases also have an inverse kinetic isotope effect, since the heavy hydroxide ion is a stronger base than the light hydroxide ion. Again, the primary isotope effect would tend to cancel this effect, *i.e.*, to make the light ion react faster.

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Photochemistry of Methoxyacetone

By R. SRINIVASAN

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Photolysis of methoxy acetone at 3130 Å. led to acetone and formaldehyde as the important products. A small amount (about 1/20th of the acetone) of carbon monoxide was the only other significant product. Although estimates of the yield of formaldehyde led to lower values than for acetone, it is likely that methoxy acetone decomposes mainly to one molecule each of acetone and formaldehyde. The quantum yield of acetone was 0.32. This value was unaffected by changes in pressure and was only slightly affected by an increase in temperature. Addition of biacetyl or nitric oxide had no observable effect. Oxygen had no effect at 105° but at room temperature a decrease in the yield of acetone was noted. It is believed that acetone (and formaldehyde) are formed by the Norrish type II intramolecular process. The effect of oxygen at room temperature may be due to changes in the surface of the walls of the reaction cell.

Introduction

The photochemistry of the simple aliphatic ketones has been extensively studied and is fairly

well understood. It seemed logical to extend this knowledge to aliphatic ketones with more than one functional group. Methoxyacetone which is