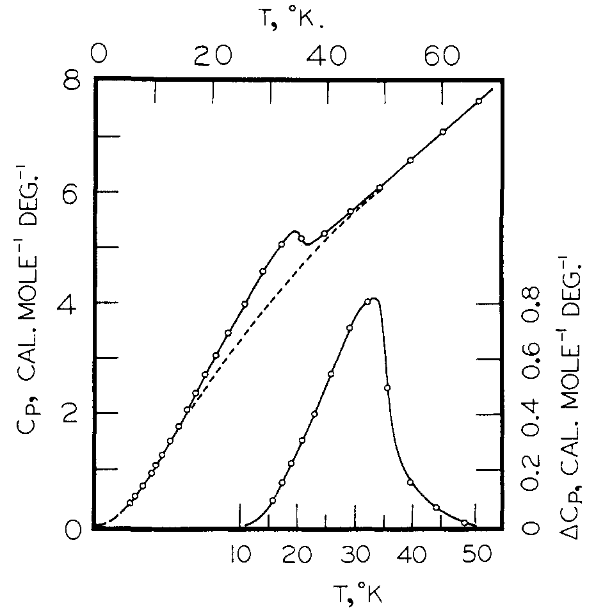

Fig. 1.—Molal heat capacity of sodium methoxide. Experimental heat capacities are plotted and resolved into the lattice contribution (dashed curve) and the anomalous portion (inset).

expressed in terms of the defined thermochemical calorie equal to 4.1840 absolute joules. The ice point was taken to be 273.16°K.

The molal heat capacity and the thermodynamic functions derived from the heat capacity are listed at rounded temperatures in Table II. These heat capacity values were read from a smooth curve through the experimental points, and they are estimated to have a probable error of 0.1% above 25°K., 1% at 10°K., and 4% at 5°K. The heat capacity was extrapolated below 6°K. with a T^3 function. The effect of nuclear spin is not included in the entropy and free energy function. The estimated probable error in the entropy, heat content and free energy function is 0.2% above 100°K., but in order to make the table internally consistent some of the values are given to one more figure than is justified by the estimated probable error.

The measured heat capacities from 5 to 70° are plotted in Fig. 1 together with an estimate of the "excess" heat capacity near 34° obtained by interpolating the temperature dependence of the Debye theta over the anomalous range. The molal enthalpy and entropy increments associated with this anomaly of unknown origin are 11.5 cal. mole^{-1} and 0.43 cal. mole^{1-} deg.$^{-1}$, respectively.

Acknowledgment.—The authors appreciate the assistance of Mrs. M. W. Klonowski with the adiabatic shield control and of Mrs. Margaret S. Anderson with the calculations.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF CALIFORNIA, BERKELEY]

Classical Partition Functions for Transition State Theory. Chlorine Atom Reactions

BY KENNETH S. PITZER

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The classical formulation of the partition function is a valid and useful approximation in calculations for activated complexes in most cases. Cases where one or both reactants consist only of very light atoms must be excepted. Examples are chosen from chlorine atom reactions. Serious discrepancies reported in the literature are eliminated.

Conventional transition state theory[1] requires a knowledge of all of the normal modes of vibration in the activated complex and their frequencies. While this method has been applied successfully to some relatively complex examples,[2] it is not easy to make good approximations for all of the vibration frequencies. The classical formulation of the partition function or phase integral has the advantage that less detailed information is required.

If we take 0.2 cal. per deg. mole as a maximum error, the classical formula for the entropy of a harmonic oscillator is valid for frequencies less than 330 cm.$^{-1}$ at room temperature, or in general for $\nu < 1.1\ T$. The frequencies associated with deviation of angular alignment of reacting groups (α in Fig. 1a) are probably near or below this value unless one of the groups consists only of hydrogen atoms or the activated complex has an unusually rigid structure. The frequency associated with deviations in distance between reacting groups (r in Fig. 1b) will also be in this range if the groups are reasonably heavy. Even if the frequencies are somewhat above the limit specified above, it may be desirable to use the classical method and then make corrections for quantum effects. This has proven to be the best method of treating the carbon skeleton motions of the n-paraffin hydrocarbons[3] even though some frequencies are above 1000 cm.$^{-1}$. In this case the equilibrium properties were being calculated, but the methods are equally applicable to kinetic problems.

The classical form of the partition function is

$$Q = \frac{q_e A}{\sigma} \int \ldots . \int e^{-V/RT}\, dx_1 \ldots . dz_n \qquad (1)$$

$$A = \left(\frac{2\pi kT}{h^2}\right)^{3n/2} \prod_{i=1}^{n} m_i^{3/2}$$

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(1) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941.

(2) D. R. Herschbach, H. S. Johnston, K. S. Pitzer and R. E. Powell, *J. Chem. Phys.*, **25**, 736 (1956).

(3) K. S. Pitzer, *ibid.*, **8**, 711 (1940); **14**, 239 (1946); W. B. Person and G. C. Pimentel, THIS JOURNAL, **75**, 632 (1953).

where σ is the symmetry number, q_e the electronic partition function, m_i is the mass of the ith atom and V is the potential energy which is a function of the coördinates $x_1 \ldots z_n$ specifying the positions of the n atoms. The partition function is integrated in a serial fashion by placing the first atom anywhere in the container, then integrating for the successive additional atoms in terms of coördinates relative to the preceding atoms. It is sometimes convenient to regard groups such as CH_3, CH_2 and CH as single atoms at this point. The early stages in this serial treatment need not concern us since they will be identical for the reactant molecule and that portion of the activated complex. Our problem is the additional factor arising for the activated complex.

Let us consider the case of reaction of a hydrocarbon R–H with a chlorine atom. The desired quantity is the ratio $Q^{\ddagger}/Q_{R-H}$ of the transition state partition function to that of the reactant hydrocarbon. We consider the additional factor introduced by the addition of the chlorine atom and the effect of released constraints on the reacting hydrogen. This calculation applies to a single reaction site, *i.e.*, C–H bond. In terms of polar coördinates about the equilibrium position of the hydrogen atom at the reaction site and fixed in the hydrocarbon molecule, this factor is

$$\frac{Q^{\ddagger}}{Q_{R-H}} = q_e \left(\frac{2\pi k T m_{Cl}}{h^2}\right)^{3/2} \iiint e^{-V(r,\theta,\phi)/kT}\, r^2 \sin\theta \, dr\, d\theta\, d\phi \qquad (2)$$

The C–H stretching mode has become the reaction coördinate. The entropy of the C–H stretching frequency is usually negligible, hence no correction need be made. The H bending frequencies for the reacting hydrogen are probably affected but it is difficult to estimate how much. Since their entropy contribution is small, it is a reasonable approximation to assume that they are unchanged and omit them also from equation 2.

Presently we shall define $V(r, \theta, \phi)$ more precisely and evaluate the integral. First, however, let us note that so long as V remains unchanged, equation 2 is the same for all hydrocarbons. Thus the pre-exponential factors for the reaction

$$R\text{-}H + Cl = HCl + R$$

for various hydrocarbons should be simply proportional to the number of hydrogen atoms constituting reaction sites. Knox and Trotman-Dickenson[4] have summarized the information on these reactions. Relative to ethane, the pre-exponential factor per hydrogen atom is 0.39 for methane, 1.10 for propane, 0.98 for isobutane and 0.50 for neopentane. These values are all close to unity within the accuracy usually expected for pre-exponential factors in reactions of this type. In these cases the stated experimental accuracy is somewhat higher and some modest differences in the potential V in equation 2 are therefore indicated. In any case no serious discrepancy exists.

The much larger discrepancies found by Knox and Trotman-Dickenson[4] arose from their assumption that vibrational entropies of activation could be ignored. The difficulties in a calculation of these terms on the conventional basis are recognized, but their magnitude is by no means negligible. We shall see below that the vibration frequencies associated with the new motions in the activated complex indicated in Fig. 1 are very low even for methane and that the corresponding entropies are large.

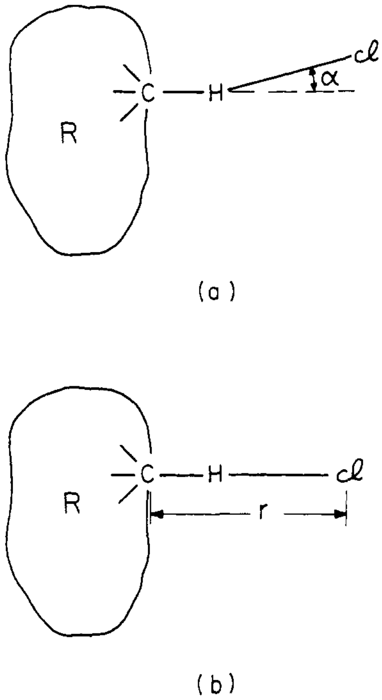

Fig. 1.—The coördinates of a chlorine atom in an activated complex for reaction with hydrocarbon R–H. α in the figure is the polar angle θ in the equations.

Hydrogen Molecule–Chlorine Atom Reaction.—Our assumption of essentially classical vibrations in the transition state where the R group moves as a unit fails when we consider the cases of H_2. Now the transition state is tri-atomic H....H....Cl and the standard quantum statistical equations are readily applied. We present the calculation briefly, however, to develop a potential function for the preceding case.

Bigeleisen and Wolfsberg[5] have applied transition state theory to the relative rates of the H_2–Cl reaction for various isotopes of hydrogen. We believe the linear complex is probably correct (instead of a bent complex). The Bigeleisen and Wolfsberg calculation was sensitive only to the frequency of stretching of the long hydrogen chlorine distance and we adopt their value of 1460 cm.$^{-1}$ for the case of light hydrogen. The asymmetric longitudinal vibration of the central hydrogen is, of course, the reaction coördinate whose frequency is zero or imaginary. The isotope effect calculations of Bigeleisen and Wolfsberg were insensitive to the bending frequency so long as it was low, hence they made an arbitrary choice. This will not suffice for our purpose. Since we have no

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[4] J. H. Knox and A. F. Trotman-Dickenson, *J. Phys. Chem.*, **60**, 1367 (1956).

[5] J. Bigeleisen and M. Wolfsberg, *J. Chem. Phys.*, **23**, 1535 (1955).

adequate basis for an accurate prediction, let us reverse the calculation and use the observed Arrhenius factor from rate data to obtain this frequency. We may then judge its reasonableness.

The interatomic distances in this activated complex are those of approximately half bonds H—H and H—Cl. Pauling's formula[6] yields an increase of 0.09 Å. for the length of a half bond above that of a single bond. This formula applies to metals and electron deficient molecules where there is little repulsive interaction between bonding electrons and unshared pairs. In the present case this sort of repulsion does arise and may be expected to increase the distances slightly. We have chosen 0.9 Å. for the H–H and 1.5 Å. for the H–Cl distances, respectively.

The remaining steps are straightforward.[7] The reaction complex has electronic spin of $^1/_2$ and a spin entropy of R ln 2. The moment of inertia is 12.6×10^{-40} g. cm.^{2} and at 600°K. the standard entropy (at 1 atm. pressure) for the reaction complex is $54.3 + S_\nu$ where S_ν is the contribution of the unknown bending frequency. The entropy[8] of H_2 is 36.08 and that of atomic Cl is 43.21. In some calculations the additional electronic entropy of Cl above the R ln 2 for spin has been overlooked. The ground $^2P_{3/2}$ state alone has R ln 4 electronic entropy and the $^2P_{1/2}$ state lies low enough in energy to make some additional contribution.

Ashmore and Chanmugam[9] showed that various data for the reaction $H_2 + Cl = HCl + H$ over the range from room temperature to 700° were consistent with the rate constant $10^{13.9}\exp(-5500/RT)$. We assign this Arrhenius factor to the middle of the temperature range or about 600°K. and find $\Delta S_{600}^{\ddagger} = -21.8$ if the standard state of 1 atm. is used. The combination of these values yields $S_\nu = 3.2$ cal./deg. mole at 600°K. or $\nu = 540$ cm.$^{-1}$ since it is a doubly degenerate vibration. This frequency appears reasonable; it is lower than normal hydrogen bending frequencies by about a factor of two.

Hydrocarbon–Chlorine Atom Reactions.—Let us now assume that the potential energy function in the reaction area is essentially the same for a C–H–Cl activated complex as for the H–H–Cl complex. The C–H distance is, of course, greater than that for H–H. Also we avoid unnecessary numerical complications by assuming that the C–H distance of the hydrocarbon remains unchanged in the activated complex, but we increase the H–Cl distance to 1.6 Å. in order to yield a more reasonable C–Cl distance. The vibration frequencies of 1460 cm.$^{-1}$ for stretching and 540 cm.$^{-1}$ for bending in the H–H–Cl case define a valence force potential function[10] of the type appearing in equation 2 which we may write as

$$\begin{aligned} 2V &= k_r(r - r_0)^2 + k_\theta\theta^2 \\ k_r &= 1.2 \times 10^5 \text{ dynes cm.}^{-1} \\ k_\theta &= 4.6 \times 10^{-13} \text{ erg radian}^{-2} \end{aligned} \qquad (3)$$

where $(r - r_0)$ is the displacement of the radial distance[11] to the Cl atom from the optimum value r_0. The optimum value of θ is zero and there is no potential dependence on ϕ.

Equation 2 now becomes

$$\frac{Q^{\ddagger}}{Q_{RH}} = g_e\left(\frac{2\pi kTm_{Cl}}{h^2}\right)^{3/2} 2\pi\int e^{-k_\theta\theta^2/2kT}\sin\theta\, d\theta \times \int e^{-k_r(r - r_0)^2/2kT}\, r^2\, dr \qquad (4)$$

We make the approximations that $\sin\theta \cong \theta$ and $(r - r_0) << r_0$ after which the integrations are straightforward and, with an electronic multiplicity of 2, yield

$$\frac{Q^{\ddagger}}{Q_{RH}} = \left(\frac{2\pi kT}{h}\right)^3\left(\frac{2m_{Cl}{}^{3/2}r_0{}^2}{k_r{}^{1/2}k_\theta}\right) \qquad (5)$$

The standard statistical thermodynamic formulas then yield

$$S^{\ddagger} - S_{RH} = R\left[3 + 3\ln\left(\frac{2\pi kT}{h}\right) + \frac{3}{2}\ln m_{Cl} + 2\ln r_0 + \ln 2 - \frac{1}{2}\ln k_r - \ln k_\theta\right] \qquad (6)$$

Insertion of the potential constants given above together with the other quantities in equation 6 yields at 400°K.

$$S^{\ddagger} - S_{RH} = 16.6 \text{ cal. deg.}^{-1} \text{ mole}^{-1} \qquad (7)$$

At this temperature the entropy of atomic chlorine is 41.01 and $\Delta S^{\ddagger}$ is -24.4 cal. deg.$^{-1}$ mole^{-1}. The pre-exponential factor, per hydrogen atom, is then 9.2×10^{12} cc. mole^{-1} sec.$^{-1}$.

Before accepting this result we must investigate the magnitude of quantum effects. Let us consider methane first. The stretching frequency is readily calculated if we assume that the CH_3 group is a single mass of 15 units; the result is 440 cm.$^{-1}$. At 440°K. this is just at the limit $1.1T$ for the small quantum correction of 0.2 cal. deg.$^{-1}$ mole^{-1}. The bending frequency is more difficult to calculate, but it may be estimated by assuming that the inertial effect is just the moment of inertia of methane. One then obtains 160 cm.$^{-1}$ and may safely conclude that quantum corrections are negligible. Quantum effects will be even smaller for heavier hydrocarbons.

The best absolute value for the pre-exponential factor for a hydrocarbon–chlorine reaction is probably that of Pritchard, Pyke, and Trotman-Dickenson[12] for methane. They reacted H_2 and CH_4 competitively and combined their result for the relative rates with that mentioned above for the absolute rate of reaction with H_2. They find $2.6 \times 10^{13}\exp(-3850/RT)$ cc. mole^{-1} sec.$^{-1}$ for the methane reaction in the range around 400°K.

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(6) L. Pauling, THIS JOURNAL, **69**, 542 (1947).

(7) We are ignoring the possible effect of tunnelling through the top of the potential barrier. In the Bigeleisen and Wolfsberg[5] calculation an estimate was included for this effect. The introduction of their assumptions here would change our numerical values slightly but would not affect any significant conclusions.

(8) "Selected Values of Chemical Thermodynamic Properties," Series III, National Bureau of Standards, Washington, D. C.

(9) P. G. Ashmore and V. Chanmugam, *Trans. Faraday Soc.*, **49**, 254 (1953).

(10) The vibrations of a linear XYZ molecule are treated by W. S. Richardson and E. B. Wilson, Jr., *J. Chem. Phys.*, **18**, 694 (1950); G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., Inc., New York, N. Y., 1945, p. 173.

(11) We are using the C–Cl force constant to apply to variations in the distance from the Cl atom to the equilibrium position of the H atom which is the origin of the coördinate system. So long as θ is small this causes no error and avoids a coördinate transformation.

(12) H. O. Pritchard, J. B. Pyke and A. F. Trotman-Dickenson, THIS JOURNAL, **77**, 2629 (1955).

Our calculated value for the pre-exponential factor is $4 \times 9.2 \times 10^{12} = 3.7 \times 10^{13}$ cc. mole^{-1} sec.$^{-1}$. The agreement is all that one should expect.

We may conclude that the pre-exponential factors in these reactions with chlorine atoms are in accord with the transition state theory. Also we found that the classical partition function yielded a good approximation for the reactions of hydrocarbons with chlorine atoms. The extension of this method to cases of other reactions of a single atom with a molecule is straightforward and will yield similar simplification of the calculations. Extension of the classical partition function to reactions between two diatomic or polyatomic molecules (or radicals) is also quite feasible.

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[CONTRIBUTION FROM THE PHYSICAL RESEARCH DIVISION, CHEMICAL WARFARE LABORATORIES]

Nuclear Magnetic Resonance Spectra of Some Fluorocarbon Derivatives

BY NORBERT MULLER,[1] PAUL C. LAUTERBUR AND GEORGE F. SVATOS

RECEIVED DECEMBER 6, 1956

The ^{19}F nuclear magnetic resonance (NMR) spectra of a number of perfluoroörganic compounds have been measured. Correlations are presented between the observed chemical shifts and the types of fluorine-containing groups present. Interpretation of the spectra often is facilitated by observing the fine structures of the resonance signals. NMR spectroscopy is an excellent source of information as to the structures and purities of new fluorocarbon derivatives.

Introduction

The usefulness of nuclear magnetic resonance (NMR) spectroscopy in determining the structures of organic and fluorocarbon molecules is now widely recognized. It is based on the fact that the chemical shift of the resonance from a proton or an F^{19}-nucleus is determined by the nature of the functional group in which the nucleus is found, although there is some overlapping of the regions containing the resonances associated with different groups. Meyer, Saika and Gutowsky[2] observed proton resonances from a large variety of organic materials, and present extensive correlations between the chemical shifts found and the natures of the proton-containing groups. As yet there is very little analogous work in the literature concerning F^{19} chemical shifts.[3-5] We are therefore presenting this account of the application of NMR spectroscopy to the identification and determination of the structures of a number of perfluoroörganic compounds prepared in these laboratories.[6]

Experimental

The apparatus used in this work differs from that previously described[7] only in that a Varian Model V-K 3506 super-high resolution field stabilizing unit has been added. The effects of field inhomogeneities were reduced by using Varian Associates' spinning attachment. The resolution obtained is illustrated in Fig. 1; the separation between the most closely spaced components of the multiplet shown is just under one milligauss.

Chemical shifts were measured by the "side-bands" technique,[8] using CF_3COOH as the source of the standard resonance. The unit employed is

$$\delta = \frac{(H_s - H_r)}{H_r} \times 10^6$$

where H_s and H_r are the resonant magnetic fields for the sample and the reference compound, respectively.[9] The measured values were reproducible to within 0.1 δ-unit, and are not corrected for bulk-diamagnetic effects.[10]

The preparations and purifications of the samples are described in reference 6. All were examined at room temperature, as liquids sealed in Pyrex tubes of 5 mm. outside diameter which were filled to a height of about 25 mm.

Results and Discussion

Assignment of the Resonances.—The δ-values of the resonances of the various fluorine-containing groups of each molecule studied are given in Table I, and the correlation between chemical shifts and types of group is summarized in Table II. The assignments were made on the basis of the fact that similar groups in different compounds should give resonances in the same region, and also the rule that the intensity of each signal is proportional to the number of resonating nuclei. The absence of any resonances which could not be accounted for in this manner is strong evidence in favor of the structures proposed for the compounds, and also indicates that at most a few mole per cent. of fluorine-containing impurities could have been present, since the possibility of a sample's containing several compounds with identical NMR spectra is rather remote. In several cases the observed spectrum formed the basis for a choice between several candidate structures.

Indirect Spin–Spin Interactions.—In a number of instances, the assignments could be confirmed by observation of the hyperfine structure resulting

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[1] Department of Chemistry, Purdue University, Lafayette, Indiana.

[2] L. H. Meyer, A. Saika and H. S. Gutowsky, THIS JOURNAL, **75**, 4567 (1953).

[3] S. Steinle, H. M. McConnell and others, volume 2 of Final Report on Contract No. CML-4564, Shell Development Company, Emeryville, California, 1954.

[4] (a) H. S. Gutowsky, D. W. McCall, B. R. McGarvey and L. H. Meyer, THIS JOURNAL, **74**, 4809 (1952); (b) J. N. Shoolery, *Anal. Chem.*, **26**, 1400 (1954).

[5] G. V. D. Tiers, THIS JOURNAL, **78**, 2914 (1956).

[6] J. A. Young, T. C. Simmons and F. W. Hoffman, *ibid.*, **79**, in press (1957); F. W. Hoffman, T. C. Simmons, *et al.*, presented at the 130th National Meeting of the Am. Chem. Soc.; R. J. Koshar, T. C. Simmons and F. W. Hoffman, presented at the 130th National Meeting of the Am. Chem. Soc.; T. C. Simmons, F. W. Hoffman, *et al.*, in preparation.

[7] N. Muller, P. C. Lauterbur and G. F. Svatos, to be published.

[8] J. T. Arnold and M. E. Packard, *J. Chem. Phys.*, **19**, 1608 (1951); see also N. Muller, P. C. Lauterbur and J. Goldenson, THIS JOURNAL, **78**, 3557 (1956).

[9] There is as yet no universally adopted convention as to the definition of δ; chemical-shift scales are in use in which the sign of the δ's is reversed, and for which different origins have been chosen. See, for example, the discussion in reference 4b.

[10] W. C. Dickinson, *Phys. Rev.*, **81**, 717 (1951).