equilibrium aqueous phase was taken, diluted so that the concentration of nitromethane was in the range of 0.025 to 0.075 *M* (with an electrolyte concentration in the range 0.02 to 0.06 *M*) and was analyzed by measuring the optical density at 270 mμ. The extinction coefficient for nitromethane in aqueous solution was found to equal 14.7 at 270 mμ and 9.51 at 246 mμ. The extinction coefficient of nitromethane was found to be unaffected by electrolyte concentration up to 0.2 *M*.

The Activity Coefficient of Aqueous Nitromethane.—The vapor pressure of nitromethane above the binary solution was determined by spectrophotometry of the saturated vapor, using a simple apparatus consisting of a silica spectrophotometer cell connected to a Pyrex solution bulb by a graded seal. An aqueous nitromethane solution of known concentration was introduced into the solution bulb, which was then frozen with liquid nitrogen to prevent the concentration of the solution from changing while the air was pumped out of the apparatus. After evacuation the solution bulb was placed in a constant temperature bath (24.8°), and after equilibration the optical density of the vapor in the silica cell (at room temp.) was measured at 220 mμ and a slit width of 0.3 mm. The optical density of the vapor over pure nitromethane at different constant temperatures was measured and it was found that nitromethane obeys Beer's law in the vapor phase from zero pressure to 39 mm. pressure: optical density = 0.0385*P* (mm.). The

$$\log_{10} P = -2423.7/T - (3.3821) \log_{10} T + 18.0571$$

equation[10] was used to compute the vapor pressure of pure nitromethane at the different temperatures. The activity coefficient of nitromethane in the solution is obtained from the equation

$$\log_{10} \gamma_0 = \log_{10} P_v/m - \log_{10} h$$

where P_v = partial pressure of nitromethane in the vapor, γ_0 = activity coefficient of nitromethane in solution, m = molal concentration of nitromethane in solution, and h is the Henry's law constant $(\lim_{m \to 0}(P_v/m))$. It is assumed here that the fugacity of nitromethane equals its partial pressure. This assumption can be justified for idealized gaseous mixtures in which the fugacity, f_v, is given by the equation

$$\ln(f_v/P_v) = (P_t/RT)B$$

where P_t is the total pressure of the mixture and B is the second virial coefficient for nitromethane vapor. B has been determined[11] as

$$-300 - 12.97e^{1700/T}(\text{cc./mole})$$

Then in the present experiments, $0.987 \leq f_v/P_v \leq 1$.

The partial pressure of nitromethane above the liquid solution from $m = 0.2$ to $m = 2.0$ is well represented by the equation

$$\log_{10} P/m = -(0.063 \pm 0.13)m + 1.362 \pm 0.009$$

Again, P is the pressure in mm. and the uncertainties are standard deviations. The slope is evidently independent of m_1 and therefore is equal to $(\partial \ln \gamma_0/\partial m_0)_{m_{0s}}/2.303$.

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[10] C. A., 34, 4316^8 (1940); E. B. Hodge, *Ind. Eng. Chem.*, **32**, 748 (1940).

[11] J. P. McCullough, D. W. Scott, R. E. Pennington, I. A. Hossenlopp and Guy Waddington, *J. Am. Chem. Soc.*, **76**, 4791 (1954).

THE REACTIONS OF CHLORINE ATOMS—A TEST OF THE TRANSITION STATE THEORY

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The relative *A* factors for reactions of the type Cl + RH = HCl + R have been calculated on the assumptions of the transition state theory. A comparison of these values with the accurate experimental data reveals considerable discrepancies.

The transition state theory of chemical kinetics has been applied with fair success to the calculation of the order of magnitude of the Arrhenius *A* factors of bimolecular reactions.[1] Little more can however be claimed for two reasons: firstly, doubtful assumptions as to the configurations of the activated complexes had to be made which led to considerable uncertainty in the calculated values, and secondly, experimental results of sufficient accuracy to sustain an unambiguous test were not available. The usual errors in the measurement of activation energies of these reactions were, under the most favorable conditions, of the order of ± 300 cal./mole. The corresponding error in the *A* factor is then $10^{\pm 0.2}$ (about ± 60%).

In the present paper, relative *A* factors calculated from transition state theory are compared with those determined experimentally by us[2,3] for the competitive reactions of chlorine atoms with several hydrocarbons. Calculated *A* factor ratios are also given for a number of reactions which have not yet been studied but which we hope to investigate in due course. These reactions of chlorine atoms offer a number of advantages for such a study. In the first place there is much less doubt about the configuration of the activated complexes in reactions of atoms than in the corresponding reactions of free radicals, there being no uncertainty about the free rotation of the radical in the former case. Secondly, the activation energies of the reactions are low and may therefore be measured with very small absolute errors (although the percentage error will be of the usual magnitude). It may furthermore be assumed that in such cases the bond lengths C–H–Cl will vary little from complex to complex and that the C–H and C–Cl bond lengths will be only slightly longer than those in normal molecules. Thirdly, by employing a competitive technique, relative *A* factors can be determined with unusual precision. In the most favorable cases relative activation energies have been measured to within 30 cal./mole giving relative *A* factors to within 5%.

These relative *A* factors can therefore provide a stringent test of the transition state theory since not only can they be measured experimentally with

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[1] A. F. Trotman-Dickenson, "Gas Kinetics," Academic Press, Inc., New York, N. Y., 1955.

[2] H. O. Pritchard, J. B. Pyke and A. F. Trotman-Dickenson, *J. Am. Chem. Soc.*, **77**, 2629 (1955).

[3] J. H. Knox, *Chem. and Ind.*, 1631 (1955).

high precision but they may also be calculated with high accuracy making use of fewer assumptions than are required in the calculation of absolute values.

According to transition state theory the relative A factors for the competitive reaction of chlorine atoms with methane and ethane are given by the equation

$$\frac{A_{\mathrm{CH_4}}}{A_{\mathrm{C_2H_6}}} = \frac{[\phi^{\mathrm{tr}}_{\mathrm{CH_4Cl}}\ \phi^{\mathrm{rot}}_{\mathrm{CH_4Cl}}\phi^{\mathrm{vib}}_{\mathrm{CH_4Cl}}]/[\phi^{\mathrm{tr}}_{\mathrm{CH_4}}\ \phi^{\mathrm{rot}}_{\mathrm{CH_4}}\ \phi^{\mathrm{vib}}_{\mathrm{CH_4}}]}{[\phi^{\mathrm{tr}}_{\mathrm{C_2H_6Cl}}\ \phi^{\mathrm{rot}}_{\mathrm{C_2H_6Cl}}\ \phi^{\mathrm{vib}}_{\mathrm{C_2H_6Cl}}]/[\phi^{\mathrm{tr}}_{\mathrm{C_2H_6}}\ \phi^{\mathrm{rot}}_{\mathrm{C_2H_6}}\ \phi^{\mathrm{vib}}_{\mathrm{C_2H_6}}]}$$

$$= \exp\left[\frac{1}{R}(\Delta S^{\mathrm{tr}}_{\mathrm{CH_4}} - \Delta S^{\mathrm{tr}}_{\mathrm{C_2H_6}} + \Delta S^{\mathrm{rot}}_{\mathrm{CH_4}} - \Delta S^{\mathrm{rot}}_{\mathrm{C_2H_6}} + \Delta S^{\mathrm{vib}}_{\mathrm{CH_4}} - \Delta S^{\mathrm{vib}}_{\mathrm{C_2H_6}})\right]$$

where the partition functions, denoted by ϕ's, are measured from the ground state of the parent molecule and of the complex, respectively. The activation energy appropriate to these theoretical A factors is therefore the activation energy at absolute zero which may be denoted ΔE°_0. The ΔS values are the entropies of activation appropriate to the translational, rotational and vibrational degrees of freedom. In the above expression for the A factors the transmission coefficients have been omitted, and the symmetry numbers are taken to be included in the rotational partition functions. If the partition functions are evaluated without the symmetry numbers the values for the A factors are those for individual hydrogen atoms. Denoting such factors by A' the above equation can be written

$$\frac{A'_{\mathrm{CH_4}}}{A'_{\mathrm{C_2H_6}}} = \left\{\frac{M_{\mathrm{CH_4Cl}}/M_{\mathrm{CH_4}}}{M_{\mathrm{C_2H_6Cl}}/M_{\mathrm{C_2H_6}}}\right\}^{3/2} \times \left\{\frac{(ABC)_{\mathrm{CH_4Cl}}/(ABC)_{\mathrm{CH_4}}}{(ABC)_{\mathrm{C_2H_6Cl}}/(ABC)_{\mathrm{C_2H_6}}}\right\}^{1/2} \times \exp\left[\frac{1}{R}(\Delta S^{\mathrm{vib}}_{\mathrm{CH_4}} - \Delta S^{\mathrm{vib}}_{\mathrm{C_2H_6}})\right]$$

where M's are the molecular weights of the various substances and the product (ABC) is the product of the moments of inertia about the three principal axes of the molecules. While the masses are known exactly, the values of (ABC) are not known with the same precision because of the slight uncertainty (probably less than 0.2 Å.) as to the C–H–Cl distances. Values of (ABC) can however be calculated to any degree of accuracy once a configuration has been accepted. Since any error in the C–H–Cl distances will affect the (ABC)'s of all complexes in the same sense and roughly in the same proportion, any error of choice will largely cancel out. There are three likely sources of error in comparing the calculated values with the experimental ones. The calculation of the vibrational entropy term is not possible with any certainty. It will however almost certainly be small. The vibrational entropies of methane and ethane are both less than 1 e.u. and the vibrational entropies of activation will therefore be much smaller than 1 e.u. Differences in vibrational entropies of activation as between say methane and ethane will be even smaller and probably not greater than ±0.1 e.u. The vibrational term which might at first sight appear to result in large uncertainty in the calculation of the theoretical A factor should not therefore contribute more than about exp $0.1/R$, that is, about 5% uncertainty.

In these calculations the contributions from internal rotations in the parent molecules and the complexes have been neglected. The appropriate allowance may readily be made only in the simplest cases where the rotators are symmetrical tops. In the case of ethane, for example, the contribution to the entropies of the parent and the complex due to free internal rotation are, ignoring the symmetry factor, 5.06 and 5.66 e.u., respectively. An error of about 30% may therefore be introduced in the particular case of ethane/methane by ignoring internal rotation. For higher homologs the contributions due to changes in internal rotation will be smaller than this. In the cases considered we are moreover concerned with restricted rotation rather than free rotation, and the effect of neglecting rotations is thus further reduced.

Lastly, there is likely to be a discrepancy between the theoretical and experimental A factors resulting from the fact that the experimental activation energy and the theoretical activation energy differ according to the equation

$$\Delta E_{\mathrm{exp}} = \Delta E_0{}^\circ + \int_0^T \Delta C_{\mathrm{v}}\,\mathrm{d}T$$

giving $$A_{\mathrm{exp}} = A_{\mathrm{calc}} \exp[(\textstyle\int \Delta C\mathrm{v}/\mathrm{d}T)/RT]$$

The difference in ΔC_{v} for two similar reactions will however be very small since the translational and rotational specific heat changes will be identical for the two reactions and only the changes in vibrational specific heats will be important. As with the vibrational entropy contributions, these will be very small indeed.

We therefore conclude that the major factors influencing the relative A factors for two similar reactions are the changes in the translational and rotational entropies. Errors of up to some 5% are introduced by ignoring the vibrational contributions, and rather more by ignoring internal rotation. The latter is however never likely to be more than about 20%, even in an extreme case such as the comparison of the chlorinations of methane and ethane.

The details of the calculations are given below and a summary of the results appears in Table I. It already has been shown[2] that A factors of the right order of magnitude may be calculated for these chlorination reactions so that considerable interest attaches to the much more accurate values found for the relative A factors. These are given in Table II where they are compared with the experimentally determined values. Examination of the table reveals that the simple transition state theory predicts only approximately the relative A factors and that the discrepancy between the calculated and the experimental values is in the sense that too large an A factor is predicted for the lighter relative to the heavier molecules except in the indirect comparison of neopentane with isobutane where the mass difference is relatively small. These discrepancies (factors of up to ten) are well without both experimental error and any reasonable estimate of the theoretical error in our calculations. They may possibly be resolved in terms of transmission coefficients which we have neglected, but as yet no general method has been suggested by which such allowance might be made. The calculations show clearly the limits of the application of the simple transition state theory, and invite further work on other series of reactions which might likewise be compared with theoretical predictions.

TABLE I

TRANSLATIONAL AND ROTATIONAL ENTROPIES

Compound	S_{trans}	Log$_{10}$ ABC^a	σ	S_{rot}
Cl	36.6	0	..	0
H_2	28.1	$\bar{1}.68^b$	2	4.1
H_2-Cl	36.8	0.89^b	1	11.0
CH_4	34.3	1.56	12	10.3
CH_4–Cl	37.8	4.29	3	19.3
C_2H_6	36.1	3.62	18	14.2
C_2H_6–Cl	38.9	5.78	3	22.7
C_3H_8	37.2	4.84	18	17.0
C_3H_8 cond.^{c}	37.2	4.65	18	16.5
p-C_3H_8–Cl (a)	39.0	6.36	3	24.0
p-C_3H_8–Cl (a) cond.	39.0	6.26	3	23.8
p-C_3H_8–Cl (b)	39.0	6.35	3	24.0
p-C_3H_8–Cl (b) cond.	39.0	6.31	3	23.9
s-C_3H_8–Cl	39.0	6.47	9	22.1
s-C_3H_8–Cl cond.	39.0	6.43	9	22.0
iso-C_4H_{10}	38.1	5.76	81	16.1
iso-C_4H_{10} cond.	38.1	5.46	81	15.4
p-iso-C_4H_{10}–Cl (a) cond.	39.5	6.91	9	23.1
p-iso-C_4H_{10}–Cl (b) cond.	39.5	6.75	9	22.7
t-iso-C_4H_{10}–Cl	39.5	6.93	81	18.7
t-iso-C_4H_{10}–Cl cond.	39.5	6.79	81	18.4
$C(CH_3)_4{}^d$	38.8	6.18	324	14.3
$C(CH_3)_4$–Cl^d	40.1	7.33	27	21.9
CF_3H	38.7	5.11	3	21.2
CF_3H–Cl	40.0	6.86	3	26.2
CCl_3H	40.1	6.88	3	26.2
CCl_3H–Cl	41.1	7.73	3	28.2

[a] Units of ABC are [molecular weight × Å.^{2}]^3. [b] These values are $\log_{10} A$ where A is the moment of inertia. [c] "cond." stands for the condensed CH_3 approximation. [d] The molecule was treated as a series of spherical shells.

TABLE II

RELATIVE A FACTORS FOR CHLORINE ATOM REACTIONS

$Cl + RH = HCl + R$

Compounds	Relative A factors/H atom A'_X/A'_Y	
X Y	Calcd.	Exptl.
Hydrogen/methane	9.8	6.3 ± 2
Methane/ethane	3.58	0.39 ± 0.03
Ethane/neopentane	5.43	2.0 ± 0.1
Ethane/chloroform	9.46	.....
Ethane/fluoroform	2.08	.....
p-Propane/*sec*-propane (a)	0.89^a; 0.82^b	0.61 ± 0.05
p-Propane/*sec*-propane (b)	0.87^a; 0.87^b	
p-isobutane/*t*-isobutane (a)	1.14^c	0.75 ± 0.1
p-isobutane/*t*-isobutane (b)	0.95^c	
	Relative A factors per molecule,^{c} A_X/A_Y	
Ethane/propane^c	1.9^a ; 1.6^b	0.68 ± 0.04
Ethane/isobutane^c	2.8^b	0.61 ± 0.04

[a] Calculated for the complete molecule. [b] Calculated using the condensed approximation. [c] These results are given in terms of the molecule as a whole because no experimental distinction was made between the different types of hydrogen atoms.

The Calculations.—Values for the translational and rotational entropies have been calculated for each of the reactants and complexes studied. The translational entropies were calculated from the Sackur–Tetrode equation; the values are given in Table I. The values obtained for the rotational entropies depend upon the precise configurations assumed for the molecules (see below). These calculations of the moments of inertia can be considerably simplified if the hydrogen atoms of the methyl groups are "condensed" into the appropriate carbon atom; each methyl group is then treated as a mass of 15 located at the center of gravity of the original methyl group. Some examples of such condensations are given in Table I, and it can be seen from Table II that this simplification yields values of the relative A factors which are only slightly different from those obtained by more laborious means.

The Configurations.—It was assumed throughout that the carbon valency angles were all equal to 109.5°. In the linear C–H–Cl groups of the activated complexes the C–H distance was taken as 1.15 Å. and the H–Cl as 1.45 Å.; other bond lengths assumed were C–C 1.54 Å., C–H *0.98* Å., C–F 1.36 Å. and C–Cl 1.76 Å. The following points may be mentioned in connection with the configurations of individual reactants and complexes.

Propane.—Calculations were made for two different configurations of the complex obtained by attack of the chlorine atom at the primary position: (a) *in which the chlorine atom in the complex* is at the greatest possible distance from the third carbon atom (*i.e.*, with the C–H–Cl bond parallel to the opposite C–C bond) (b) in which the chlorine atom is as close as possible to the third carbon atom.

Isobutane.—Calculations were again made for two configurations of the complex: (a) in which the chlorine atom was at the greatest possible distance from the tertiary hydrogen atom (*i.e.*, the C–H–Cl bond parallel to the tertiary C–H bond); (b) in which the chlorine atom is as close as possible to the tertiary hydrogen atom.

Neopentane.—This molecule was treated as a central atom of mass 12 surrounded by two spherical shells one of mass 48 and radius 1.54 Å. and the other of mass 12 and radius 2.20 Å.; the chlorine atom in the complex was taken to be a distance of 3.65 Å. from the central carbon atom.