

DIMERIZATION OF SMALL RADICALS*

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Absolute values of equilibrium constants were calculated for the dimerization reactions of methyl, formyl, and amidogen radicals. Reaction enthalpies were evaluated from the heats of formation given by the MINDO/2 method and the entropy changes were obtained by the statistical-thermodynamic treatment.

Predictions of absolute values of equilibrium and rate constants of chemical reactions represent one of the most important goals of chemical applications of methods based on quantum and statistical mechanics. If enthalpy changes are estimated by means of semiempirical methods^{1,2}, calculations of gas-phase equilibrium constants appear to be straightforward. Of course, the properties of all components should be near those of an ideal gas, which is a necessary condition for accurate predictions of entropy changes by the statistical-thermodynamic treatment³.

With SCF *ab initio* calculations the situation is complicated by the correlation energy which makes any general theoretical approach to heats of reaction prohibitive, in particular for reactions where a chemical bond is formed or broken. Satisfactory results have been obtained only for certain types of reactions having closed shell reactant and product molecules^{4,5}. However, the progress in deriving semiempirical procedures for estimation of correlation energy in closed shell molecules gives rise to hope that the SCF *ab initio* calculations will provide rather good heats of reaction in the near future. Rate processes in the gas phase are more difficult to treat. In the first place, the use of the theory of absolute reaction rates may not be always justifiable, and, second, the calculation even of several profiles of an energy hypersurface is very expensive of computer time. Here the combination of systematic calculations with chemical intuition is still desirable. Attempts to calculate interaction energies between particles in the condensed phase^{6,7} give rise to hope that reasonable theoretical estimates of enthalpies of equilibrium processes in solution will be soon available. Concerning the partition functions, the situation appears to be less favourable. A theoretical approach to rate processes in solution is a difficult task, one of the problems being the uncertain structure of the solvation shell of activated complexes.

* Part I in the series Calculations of Absolute Values of Equilibrium and Rate Constants.

TABLE I

Observed and MINDO/2 Enthalpy Data (in kcal/mol) on the Dimerization Reactions Studied (Standard State at 1 atm Pressure)

Reaction	Monomer		
	$\Delta H_f^0, 298$ (obsd.)	$\Delta H_f^0, 298$ (calc.)	$H_{298}^0 - H_0^0$
$2 \text{CH}_3 \rightleftharpoons \text{C}_2\text{H}_6$	34.0 ^a	23.490 33.5 ^b	2.432
$2 \text{NH}_2 \rightleftharpoons \text{N}_2\text{H}_4$	40.1 ^d	35.794	2.373
$2 \text{HCO} \rightleftharpoons \text{C}_2\text{H}_2\text{O}_2$	8.0 ^e	0.518	2.387

In the last five years, enthalpy changes have been calculated by quantum chemical methods for a series of reactions (*e.g.* refs.⁸⁻¹³) but calculations on entropy changes were rather rare. In contrast, in 1940-1960 entropy changes were calculated for many reactions by statistical-thermodynamic methods (*e.g.* ref.¹⁴). At that time, however, reaction enthalpies of more complex processes were difficult to calculate. Today the standard gas phase entropies, obtained by routine calculations, have been tabulated (*e.g.* ref.¹⁵).

This paper concerns the calculation of absolute values of equilibrium constants for gas phase coupling reactions (A)-(C)



making use of experimental data only to a minimal extent. Radical dimerizations of this type are important in the higher layers of the atmosphere and in various combustion processes.

CALCULATIONS

Equilibrium constants were calculated by a standard statistical-thermodynamic procedure, a brief description of which is given in the Appendix. Here we only specify molecular constants necessary for the construction of partition functions. The molecular geometries employed are those listed in Appendix B, but without an offset for C-H and N-H bond lengths required in a MINDO/2 treatment. With all three dimers under study, hindered internal rotation around the central bond is to be expected. Up to now, however, neither experimental evidence nor MO calculations¹⁶ provide a satisfactory description of the potential barrier with N_2H_4 and $\text{C}_2\text{H}_2\text{O}_2$. Hence the partition function for hindered internal rotation (see Appendix A) was constructed solely for C_2H_6 , where the potential barrier is well known¹⁷. With the other two systems, we pro-

TABLE I
(Continued)

Dimer			Reaction enthalpy		
$\Delta H_{f,298}^0$ (obsd.)	$\Delta H_{f,298}^0$ (calc.)	$H_{298}^0 - H_0^0$	$\Delta H_{r,298}^0$ (obsd.)	$\Delta H_{r,298}^0$ (calc.)	$\Delta H_{r,0}^0$
-20.2 ^c	-22.547	2.867	-88.2	-69.527	-67.530
	-20.18 ^b			-87.180 ^b	-85.183 ^b
22.79 ^d	17.032	2.755	-57.41	-54.556	-52.565
-50.66 ^f	-57.391	3.254	-66.6	-58.427	-56.907

^a Ref.²⁴. ^b MINDO/1 value²⁵. ^c Ref.²⁶. ^d Ref.¹⁵. ^e Ref.²⁷. ^f Ref.²⁸.

ceeded as recommended in ref.¹⁵ for N_2H_4 , viz. the entropy was increased by $R \ln 2$ to allow for the presence of two rotameric forms. In the construction of vibrational partition functions, we used the known vibrational frequencies of NH_2 (ref.¹⁵), N_2H_4 (ref.¹⁵), C_2H_6 (ref.¹⁸), HCO (ref.¹⁹), and $C_2H_2O_2$ (ref.²⁰). Since experimental data for CH_3 are missing, we estimated the frequencies of planar modes by the Wilson matrix analysis, adopting the force constants of methane²¹. We arrived at the following values (in cm^{-1} , degeneracy given in parentheses): 1605 (2), 2913, 3098 (2). The out-of-plane deformation fundamental ($755 cm^{-1}$) was evaluated from the force constant provided by the CNDO/2 calculations²². We used this rather than the observed value²³ since the frequencies of the other modes were also obtained theoretically. In electronic partition functions for NH_2 and HCO , the first electronic transition energies¹⁹ were taken into account; with other systems the excited states were disregarded.

RESULTS AND DISCUSSION

Table I comprises the observed and calculated heats of formation both for monomers and dimers, the $H_{298}^0 - H_0^0$ terms, and the reaction enthalpies. Before discussing the agreement between calculated and observed enthalpy data, one should consider the present situation with regard to heats of formation of radicals, e.g. the formyl radical. Here the suggested experimental value, 8 kcal/mol, was obtained²⁷ by analysis of recently reported values: -4 to -9; -3; 0; 8; 11; and 16 kcal/mol. In light of these data the calculated value, 0.5 kcal/mol, appears to be very reasonable. We think that the entries in Table I represent the limits attainable by the present semiempirical methods.

With CH_3 the MINDO/1 data are superior to the MINDO/2 data and were therefore employed in subsequent calculations on equilibrium constants. The calculated temperature dependence of these constants is given in Table II. The observed equilibrium constant²⁹ concerns the dimerization of methyl at 1000 K, its logarithm

being -10.92 . The agreement with the predicted value, -10.59 , is encouraging. With hydrazine the observed data only allow qualitative conclusions. The calculated equilibrium constants in the 1000 K range explain why it is possible to generate³⁰ NH_2 radicals at 900–1150 K.

Since no other data are available on these equilibrium constants, we made use of the experimental data on the following thoroughly studied radical coupling reactions (D)–(G):



Unfortunately the equilibrium constants could not be estimated because of difficulties encountered in calculating enthalpy terms. These difficulties are worth mentioning. With the nitric oxide dimer neither the MINDO/2 (ref.³¹) nor the *ab initio*^{32,33} calculations reproduce the observed structure³⁴ of a weakly bonded dimer with NN bond length as long as 2.4 Å. Theory predicts here a strongly bonded dimer with

TABLE II

Calculated Temperature Dependence of Equilibrium Constants, $K_p = p_{x_2}/p_x^2$, (atm^{-1}), for Reactions (A)–(C)

T, K	log K_p		
	$2 \text{CH}_3 \rightleftharpoons \text{C}_2\text{H}_6$	$2 \text{NH}_2 \rightleftharpoons \text{N}_2\text{H}_4$	$2 \text{HCO} \rightleftharpoons \text{C}_2\text{H}_2\text{O}_2$
100	181.173	110.278	118.096
200	86.951	51.665	54.900
300	55.304	31.888	33.676
400	39.389	21.925	23.019
500	29.802	15.927	16.615
600	23.398	11.927	12.346
700	18.819	9.074	9.303
800	15.386	6.941	7.027
900	12.719	5.288	5.262
1 000	10.587	3.971	3.857
1 500	4.232	0.078	-0.306
2 000	1.099	-1.809	-2.328
2 500	-0.751	-2.904	-3.505

a short NN bond. Reaction (E) represents the coupling reaction that has been studied most thoroughly. Unfortunately, MINDO/2 fails drastically for the heat of formation of NO_2 (obsd. 8.1, calc. -10.9 kcal/mol). Disappointing results were also obtained with the reaction (F), where MINDO/2 gives the value -110.2 kcal/mol for the reaction enthalpy corrected for the zero-point energy. Using the molecular constants for CN and C_2N_2 from refs^{35,40} the statistical-thermodynamical treatment of the equilibrium constant observed³⁶ at 1515 K leads to the value -139.2 kcal/mol. Finally, concerning the reaction (G) the MINDO/2 method does not permit the treatment of molecules possessing NF bonds.

APPENDIX

A) Statistical-Thermodynamic Treatment

By statistical-thermodynamic methods changes in all thermodynamical functions of an ideal gas may be calculated merely by means of the partition function

$$Q = \sum_i g_i \exp\left(-\frac{\varepsilon_i - \varepsilon_0}{kT}\right), \quad (1)$$

where ε_i is the energy of a molecule in the i state, g_i is the degeneration factor of that state, and ε_0 is the zero-point energy of the molecule. The equilibrium constant, K_p , of a chemical reaction for components A_j considered as ideal gases, can also be expressed in terms of partition functions:

$$\sum_j \nu_j A_j = 0; \quad K_p = \prod_j p_j^{\nu_j}, \quad (2)$$

$$K_p = \prod_j (Q_j^0/N_A)^{\nu_j} \exp(-\Delta H_0^0/RT). \quad (3)$$

Here ν_j is a stoichiometric factor for a reactant A_j , p_j is its partial pressure in the equilibrium mixture, ΔH_0^0 stands for the reaction enthalpy at absolute zero, Q_j^0 is a partition function (1) for the A_j component at the standard pressure ($p = 1$ atm), and N_A is the Avogadro number. The standard enthalpy change on going from any temperature to absolute zero can be evaluated from the partition function by use of the following formula³⁷

$$H_T^0 - H_0^0 = RT^2(\partial \ln Q^0/\partial T)_p. \quad (4)$$

On inserting ΔH_{298}^0 calculated by the MINDO/2 method (see the following section) into Eq. (4), the theoretical ΔH_0^0 values were obtained.

The partition functions were constructed in the simplest way, considering independent individual motions of a molecule and making use of the simple quantum mechanical models (rigid rotator, harmonic oscillator) for estimations of energy levels. In this treatment the total partition function can be expressed as a product

$$Q^0 = Q_{\text{tr.}}^0 \cdot Q_{\text{rot.}} \cdot Q_{\text{vib.}} \cdot Q_{\text{elec.}} \quad (5)$$

where for the translational Q_{tr}^0 , rotational $Q_{rot.}$, vibrational $Q_{vib.}$, and electronic $Q_{elec.}$ partition functions the following familiar expressions hold

$$Q_{tr.}^0 = \frac{(2\pi mkT)^{3/2}}{h^3} RT, \quad (p = 1 \text{ atm}) \quad (6)$$

$$Q_{rot.} = \frac{1}{\sigma} \left[\frac{8\pi IkT}{h^2} + \frac{1}{3} + \frac{1}{15} \frac{h^2}{8\pi^2 IkT} + \frac{4}{315} \left(\frac{h^2}{8\pi^2 IkT} \right)^2 \right], \quad \text{linear}^{38} \quad (7)$$

$$Q_{rot.} = \frac{(\pi I_A I_B I_C)^{1/2}}{\sigma} \left(\frac{8\pi^2 kT}{h^2} \right)^{3/2}, \quad \text{nonlinear} \quad (8)$$

$$Q_{vib.} = \prod_i \frac{1}{1 - \exp(-h\omega_i/kT)}. \quad (9)$$

Here m is the mass of a particle, I, I_A, I_B, I_C are principal moments of inertia, σ is the symmetry number, and ω_i are (harmonic) normal modes of vibration. The $Q_{elec.}$ partition function is evaluated through summation (I). If the excited states lie higher (of the order 10^4 cm^{-1} above the ground state), it is sufficient to put $Q_{elec.}$ equal to the statistical weight of the ground electronic state. For molecules with hindered internal rotation, where the potential energy dependence on the angle of rotation α can be approximated by the formula

$$V = V_0/2(1 - \cos n\alpha), \quad (10)$$

the corresponding torsional mode of vibration $\omega_{tors.}$ was replaced in the partition function by the hindered rotation³⁹

$$Q_{i.r.} = \frac{(2\pi kT I_{red.})^{1/2}}{h} \frac{n}{\sigma} \int_0^{2\pi/n} \exp\left(-\frac{V_0(1 - \cos n\alpha)}{2kT}\right) d\alpha \times \\ \times \frac{h\omega_{tors.}}{kT} \frac{1}{1 - \exp(-h\omega_{tors.}/kT)} \quad (11)$$

where n is the number of minima on the potential energy curve, $I_{red.}$ is the reduced momentum of inertia for the rotating group, and σ is its symmetry number. All other contributions to the energy of molecule were neglected. In these calculations the set of fundamental physical constants⁴⁰ and atomic masses⁴¹ was employed.

B) Calculations of Heats of Formation

Heats of formation necessary for estimates of reaction enthalpies were calculated by the MINDO/2 method², which in treating radicals was combined with the open shell method of Longuet-Higgins and Pople⁴². We employed the available experimental geometries, correcting the C—H and N—H bonds for 0.1 Å offsets as required by the MINDO/2 method: CH₃ (ref.¹⁹), $r(\text{CH}) = (1.079 + 0.1) \text{ \AA}$, $\sphericalangle \text{HCH} = 120^\circ$; C₂H₆ (ref.¹⁹), $r(\text{CH}) = (1.091 + 0.1) \text{ \AA}$, $r(\text{CC}) = 1.536 \text{ \AA}$, $\sphericalangle \text{HCH} = 108^\circ$; NH₂ (ref.¹⁹), $r(\text{NH}) = (1.024 + 0.1) \text{ \AA}$, $\sphericalangle \text{HNH} = 103.4^\circ$; N₂H₄ (ref.⁴³), $r(\text{NN}) = 1.449 \text{ \AA}$, $r(\text{N—H}) = (1.022 + 0.1) \text{ \AA}$, $\sphericalangle \text{HNH} = 106^\circ$, $\sphericalangle \text{NNH} = 112^\circ$, dihedral angle 90° ;

HCO (ref.¹⁹), $r(\text{CH}) = (1.11 + 0.1) \text{ \AA}$, $r(\text{CO}) = 1.22 \text{ \AA}$, $\sphericalangle \text{HCO}^* = 131.2^\circ$; OHCCO *trans*⁴⁶, $r(\text{CC}) = 1.525 \text{ \AA}$, $r(\text{CH}) = (1.116 + 0.1) \text{ \AA}$, $r(\text{CO}) = 1.207 \text{ \AA}$, $\sphericalangle \text{CCO} = 121.2^\circ$, $\sphericalangle \text{HCO} = 126.6^\circ$.

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* Here we used the value obtained from INDO calculations⁴⁴ because there is evidence⁴⁵ that the value of valence angle is somewhat higher than that observed by Herzberg¹⁹.

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