Computations and Estimates of Rate Coefficients for Hydrocarbon Reactions of Interest to the Atmospheres of the Outer Solar System

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The rate coefficients, including Arrhenius parameters, have been computed for a number of chemical reactions involving hydrocarbon species for which experimental data are not available and which are important in planetary atmospheric models. The techniques used to calculate the kinetic parameters include the Troe and semiempirical bond energy–bond order (BEBO) or bond strength–bond length (BSBL) methods

INTRODUCTION

A major limitation in the construction of an accurate atmospheric model is the availability of photochemical and kinetic data, with rate coefficients being the principal desideratum. However, it is impractical to supply all of the model's kinetic needs by laboratory investigation, except for those reactions to which the model is especially sensitive. Moreover, as in the case of the outer solar system, the kinetic parameters, temperature, and pressures, are often not accessible under normal laboratory conditions, or the reaction species of interest may not be suitable for study by standard experimental methods.

There are a number of theoretical and semiempirical techniques that can be used for computing approximately the rate coefficients for simple reactions. In this paper we shall employ the BEBO (bond energy–bond order), BSBL (bond strength–bond length),

and the Troe methods to calculate the reaction rates of reactions important for the chemistry of the atmospheres of the planets in the outer solar system.

ABSTRACTION REACTIONS

The technique for estimation of activation energies for simple atom transfer reactions was developed by Johnston and coworkers (1963, 1966). The method is based upon the concept of conservation of bond order during the reaction process. Here bond order is defined as a number which is related to the strength of the chemical bond, hence bond energy–bond order (BEBO). In this notation the carbon–carbon bond is of order 3 in acetylene, order 2 in ethylene, and order 1 in ethane. It is assumed, in the BEBO methodology, that as one bond is broken during a chemical reaction another is formed and that the sum of the bond orders for the two bonds, the formed and broken bond, remains constant. Empirical relationships between bond lengths, dissociation energies, and vibrational frequencies have been developed and used in the BEBO formulation to describe

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the energetics of the transition complex and of the bonds involved in the reaction.

The model is sufficiently sophisticated to recognize that the H atom involved in the transfer between donor molecule AH and acceptor radical B must be bonded to both simultaneously with a bond order of less than unity for each during the reaction. The bonding requires the electron spin of the two groups (A and B) to be parallel. The parallel spins will cause an electrostatic repulsion (the so-called triplet repulsion energy) which is considered in the description of the configuration of the transition complex in the BEBO formalism. The details of the BEBO method and its theoretical underpinnings have been described recently by Brown (1981).

In several classes of reaction, particularly those which involve H-atom abstractions by groups with high electron affinities, the activation energy derived from a BEBO calculation is often 5–7 kcal/mole larger than the experimental value. Those examples, where BEBO is less than satisfactory, include abstractions by both halogen atoms as well as hydrocarbon radicals where multiple bonded carbon is attached to the H atom either before or after reaction. In these cases, a more recent adaptation developed by Bérces and Dombi (1980a) called bond strength–bond length (BSBL) has been used to predict activation energies. Particularly in those cases where the BEBO is inadequate, BSBL has provided much more satisfactory activation energies which are in better agreement with experimental data, where they exist (Bérces and Dombi, 1980b; Brown and Laufer, 1981).

A major difference between the BEBO and BSBL approach is the treatment of the repulsion between the reacting groups to which the transferable H atom is attached. BSBL considers whether either group possesses a large electron affinity; if so, the repulsion between the two groups would be reduced since the electron used in pairing to the H atom could be attracted to the "end group" with the high electron affinity.

BEBO does not consider the electron affinity of the end groups with the concomitant reduction in repulsion and tends to predict a "looser" activated complex. The similarity between the two methods is the assumption that the atom transfer occurs through a linear transition state in agreement with quantum mechanical calculations for the simple H-atom transfer in the reaction of H_a + H_bH_c = H_aH_b + H_c.

Although the activation energies predicted by the two methods are substantially different, the preexponential (Arrhenius A factor) terms predicted by the methods are comparable and are derived from absolute reaction rate and transition state theory (Brown, 1981).

In the present work, the atom transfer reactions which are of importance are the H-atom abstractions from H_2, CH_4, and C_2H_6 by both triplet vinylidene ($H_2C = C$) and vinyl (C_2H_3) radicals. Both are unsaturated hydrocarbon radicals where use of the BSBL technique is more appropriate. The input data required for the calculation, bond lengths, bond energies, and vibrational frequencies for the C–H stretch have been described for the H-atom abstraction from CH_4 by both $H_2C = C$ and C_2H_3 (Laufer and Yung, 1983). The results of the calculations are given in Table I.

There are no direct experimental literature values with which to compare the calculated rate parameters. Based upon an estimate for the reverse reaction and a determination of the equilibrium constant, Benson and Haugen (1967) have suggested the rate for R1 is $1.3 \times 10^{-11} \exp(-4700/T)$ compared to the BSBL estimate of $1.7 \times 10^{-12} \exp(-4250/T)$ cm^{3}mole^{-1} sec^{-1}. The agreement between the two values is quite satisfactory. The differences in E_a of less than 1 kcal/mole and preexponential of a factor of less than 8 are probably extreme examples of the errors to be expected. We estimate the inaccuracy in preexponential of about a factor of 2–3 and 1 kcal/mole in the activation energy.

The rate calculated by the BSBL tech-

TABLE I

ABSTRACTION REACTIONS[a]

	Reaction		Reference
R1	$C_2H_3 + H_2 \rightarrow C_2H_4 + H$	$k_1 = 1\ 7 \times 10^{-12}e^{-4250/T}$	This work
R2	$C_2H_3 + CH_4 \rightarrow C_2H_4 + CH_3$	$k_2 = 5 \times 10^{-13}e^{-4350/T}$	Laufer and Yung (1983)
R3	$C_2H_3 + C_2H_6 \rightarrow C_2H_4 + C_2H_5$	$k_3 = 1\ 6 \times 10^{-12}e^{-3200/T}$	This work
R4	$H_2C_2 + H_2 \rightarrow C_2H_3 + H$	$k_4 = 2\ 5 \times 10^{-12}e^{-3150/T}$	This work
R5	$H_2C_2 + CH_4 \rightarrow C_2H_3 + CH_3$	$k_5 = 5 \times 10^{-13}e^{-2750/T}$	Laufer and Yung (1983)
R6	$H_2C_2 + C_2H_6 \rightarrow C_2H_3 + C_2H_5$	$k_6 = 1\ 6 \times 10^{-12}e^{-2300/T}$	This work
R7	$H_2C_2 + C_2H_4 \rightarrow C_2H_3 + C_2H_3$	$k_7 = 1\ 1 \times 10^{-12}e^{-2450/T}$	This work

[a] Arrhenius parameters obtained from a BSBL calculation. Input data from all reactions from Laufer and Yung (1983). Molecular units are used throughout In Table I, all reactions are second order with units of cm^3 molecule^{-1} s^{-1}

nique and reported in Table I represents only one possible reaction channel, abstraction. Other pathways such as insertion followed by decomposition of the adduct are specifically not included in the model.

THREE-BODY COMBINATION REACTIONS

Troe (1977a,b, 1979) has promulgated a formulation of simplified computational methods for unimolecular rate coefficients, derived from the more exact quantum-statistical theory of Rice, Ramsperger, Kassel, and Marcus (Marcus and Rice, 1951; Marcus, 1952; Rice, 1961). Although the Troe formulation has recently gained wide acceptance in the area of theoretical kinetics, it has not been applied to planetary modeling. The recent recognition that collisional effects in energy transfer processes do not necessarily involve large energy jumps (the strong collision approximation) required the addition of weak collision effects to unimolecular rate theory. Troe has derived expressions which include weak collision parameters yet retain the accuracy of the RRKM formalism for determination of the low-pressure rate constant. The Troe version, statistical in nature, permits the separation of the low-pressure rate constant into a number of factors each of which may be calculated separately and their contributions determined. We believe that some

combination of theoretically calculated (using the Troe formulation) rate coefficients with experimentally derived values represents the optimum means of satisfying the needs of planetary models.

Thermal unimolecular reactions exhibit a pressure dependence modulated by competition between the intramolecular redistribution of energy and its transfer via intermolecular collisions. In the limiting low pressure region, the reaction rate is determined by the collisional transfer of energy between the excited species and the bath gas molecules. At higher pressures and hence increasing densities of the bath gas, intramolecular rearrangement becomes more competitive and is the dominant factor in the high pressure limit. The pressure range between these two extremes, where the reaction rate is determined by some combination of the two processes, commonly is referred to as the "falloff" region.

The usual approach to the calculation of unimolecular rate coefficients is, first, to treat the low- and high-pressure limits (k_0 and k_∞, respectively) as separate solutions; and, second, to obtain the falloff rate coefficient (k) by interpolation between k_0 and k_∞, of which the Lindemann–Hinshelwood expression is the simplest example,

$$k = \frac{k_0 k_\infty}{k_0 M + k_\infty}.$$

Our approach follows this pattern in as much as we utilize the Troe formulation for calculating k_0, and supply k_∞ from another source (usually based on experiment).

According to Troe (1977a,b), the rate constant (k) for combination in the low pressure limit is given by

$$k = k_{rec,0}/M = \beta_c k_{rec,0}^{sc}/M$$
$$= \beta_c K_{eq}^{-1} k_0^{sc}/(Me^{-E_0/kT})$$

where

M = bath gas concentration (= Ar in this work)

β_c = weak collision efficiency,

K_{eq} = equilibrium constant,

k_0^{sc} = strong collision rate constant.

The strong collision rate constant can be calculated from the following expression

$$k_0^{sc} = MZ_{LJ}\frac{\rho_{vib,h}(E_0)kT}{Q_{vib}}\exp(-E_0/kT)$$
$$\times F_{anh}F_eF_{rot}F_{rot,int}$$

with

Z_{LJ} = Leonard–Jones collision frequency,

Q_{vib} = the vibrational partition function,

$\rho_{vib,h}(E_0)$ = the harmonic oscillator density of states,

F_{anh} = the anharmonicity factor for Morse oscillators,

F_e = the energy dependence factor,

F_{rot} = the rotational factor,

$F_{rot,int}$ = the internal rotation factor.

The mathematical expression for each of the factors has been provided by Troe (1977a,b). A number of hydrocarbon reactions were studied using this formalism. Table IIa presents a summary of the details of the computations at 300°K, assuming that the torsion mode can be ignored. The results for R8 and R9 are similar to those obtained by Troe (1977b). The results for

R10–R13 are new. Table IIb summarizes an extended set of calculations for R8–R13 for temperatures 100, 200, and 300°K for cases including and excluding the torsion mode. On the basis of a comparison between calculation and experimental data for C_2H_6 (see Troe, 1977b), we conclude that rate coefficients calculated without the torsion mode are more realistic. The Troe calculation for R13 is strictly speaking invalid, because the reaction is likely to have a substantial activation energy. To remedy this deficiency, we modify the calculated rate coefficient by a factor of $\exp(-1000/T)$. The computed rate constants, together with those derived from experiments, are used for estimating the rate constants of a wide class of reactions. These estimates are made by analogy or on the basis of the number of degrees of freedom of the reactants and products (Williams, 1971). The results are summarized in Table IIc. It may be anticipated that certain of the reactions, particularly those radical–radical combinations, which involve CH_2 or C_2H as reactant will result in chemical activation of the product. Under these conditions the reaction "adduct" may undergo unimolecular decomposition through the most exothermic path which is not necessarily the reverse reaction. For many of these processes the rate constants have been estimated by analogy and refinement of the estimate into various decomposition channels is not warranted.

Application of the calculations to atmospheric models must be done with care. The magnitude of the calculated values might suggest an effective second order rate constant which may be greater than the collision rate; clearly a nonrealistic view. Based upon the combination of CH_3 radicals for which the high pressure limit has been well characterized, particularly at elevated temperature (MacPherson et al., 1983), estimates for the other radical–radical combination high-pressure limits may be deduced. The caveat, then, is that the three-body reaction rate is not to be used at

pressures in excess of the estimated high-pressure limit.

The Disproportionation to Combination Ratio

The large values obtained for the three-body recombination rate constants for hydrocarbon synthesis reactions shown in Table IIc suggest that the rate of formation of higher hydrocarbons is extremely efficient, even in the mesosphere. In fact, most of the three-body rate constants are so large that the limiting factor is the disproportionation to combination ratio in the two-body limit.

The disproportionation to combination ratios (r) for alkyl radicals have been extensively studied, and appear to fit a rather simple pattern (Konar, 1970; Borrell and Platt, 1970; Terry and Futrell, 1967; LaLonde and Price, 1971), as summarized in Table III. The ratios r for C_2H_3 have been deduced by Takita et al. (1968) and Christianson et al. (1975). They are considerably higher than those for alkyl radicals. We make the conjecture that vinyl–alkyl reactions are intermediate in character between alkyl–alkyl and vinyl–vinyl reactions, and that the radicals C_3H_3 and C_3H_5 are similar

TABLE IIa

CONTRIBUTING FACTORS TO RECOMBINATION RATE CONSTANT[a]

Reaction[b]	$\delta_{vib}(E_0)$ ((kcal mole^{-1})$^{-1}$)	Z_{LJ} (cm^3 molecule^{-1} s^{-1})	F_c	F_{rot}	$F_{rot\,int}$	Q_{vib}	$\dfrac{k_0^{sc}}{M_e^{-E_0/kT}}$ (cm^6 molecule^{-2} s^{-1})	β_c	$k_{rec\,0}/M$ (cm^6 molecule^{-2} s^{-1})
R8 $CH_3 + H \xrightarrow{M} CH_4$	$1\,92 \times 10^5$	$2\,17 \times 10^{14}$	$1\,04$	$40\,3$	$1\,00$	$1\,00$	$1\,84 \times 10^{21}$	$0\,27$	$6\,90 \times 10^{19}$
R9 $2CH_3 \xrightarrow{M} C_2H_6$[c]	$9\,54 \times 10^8$	$2\,24 \times 10^{14}$	$1\,08$	$21\,1$	$11\,0$	$1\,42$	$2\,69 \times 10^{25}$	$0\,43$	$5\,22 \times 10^{22}$
R10 $CH_3 + C_2H_5 \xrightarrow{M} C_3H_8$[c]	$5\,55 \times 10^{12}$	$2\,42 \times 10^{14}$	$1\,12$	$15\,3$	$8\,04$	$2\,81$	$4\,41 \times 10^{28}$	$0\,45$	$6\,87 \times 10^{24}$
R11 $CH_3 + C_3H_7 \xrightarrow{M} C_4H_{10}$[d]	$2\,24 \times 10^{16}$	$2\,34 \times 10^{14}$	$1\,15$	$12\,5$	$6\,18$	$8\,79$	$3\,44 \times 10^{31}$	$0\,46$	$2\,39 \times 10^{27}$
R12 $2C_2H_5 \xrightarrow{M} C_4H_{10}$	$1\,05 \times 10^{16}$	$2\,34 \times 10^{14}$	$1\,16$	$12\,1$	$5\,96$	$8\,79$	$1\,51 \times 10^{31}$	$0\,46$	$1\,30 \times 10^{26}$
R13 $CH_2 + C_2H_2 \xrightarrow{M} CH_3C_2H$[e]	$4\,91 \times 10^{16}$	$2\,58 \times 10^{14}$	$1\,07$	$27\,0$	$3\,93$	$1\,81$	$5\,98 \times 10^{26}$	$0\,50$	$7\,30 \times 10^{24}$

[a] Torsion mode is excluded from these computations

[b] Unless otherwise stated, the thermodynamic data are taken from JANAF (1971) and Troe (1977b), the molecular vibrational frequencies from Shimanouchi (1972), the Lennard–Jones parameters from Reid et al (1977)

[c] Thermodynamic data from Chao et al (1973) and Soviet data

[d] Thermodynamic data from Chen et al (1975)

[e] Thermodynamic data from Ziomek and Cleveland (1949)

TABLE IIb

	k (exclude torsion)			k (include torsion)		
	100°K	200°K	300°K	100°K	200°K	300°K
R8	$1\,56(-27)$	$1.72(-27)$	$1\,90(-28)$	$2\,92(-27)$	$3.23(-27)$	$3\,56(-28)$
R9	$9\,49(-24)$	$1\,32(-23)$	$1\,44(-25)$	$8.74(-23)$	$1\,22(-22)$	$1.33(-24)$
R10	$3.06(-21)$	$5\,57(-22)$	$1.89(-23)$	$2\,41(-20)$	$4\,41(-21)$	$1.49(-22)$
R11	$9.04(-19)$	$2.53(-19)$	$6\,59(-21)$	$5\,96(-18)$	$1\,67(-18)$	$4\,33(-20)$
R12	$5\,43(-20)$	$2\,90(-21)$	$3\,58(-22)$	$3\,47(-19)$	$1\,86(-20)$	$2\,31(-21)$
R13	$2\,31(-22)$ $[1\,05(-26)]$	$5\,63(-23)$ $[3.79(-25)]$	$2.01(-23)$ $[7\,17(-25)]^a$			

Notes. Rate coefficients for recombination reactions at $T = 100$, 200, and 300°K for cases excluding and including the torsion mode. Note that the rate coefficients are in units of cm^6 molecule^{-2} s^{-1}, and that CH_3C_2H does not have a torsion mode

[a] Obtained by multiplying the previous row by $e^{-1000/T}$.

TABLE IIc

	Reaction	$k(200°K)$	Source or estimate
R8	$CH_3 + H \xrightarrow{M} CH_4$	1.7×10^{-27}	Table IIb
R9	$2CH_3 \xrightarrow{M} C_2H_6$	$1\ 3 \times 10^{-23}$	Table IIb
R10	$CH_3 + C_2H_5 \xrightarrow{M} C_3H_8$	5.6×10^{-22}	Table IIb
R11	$CH_3 + C_3H_7 \xrightarrow{M} C_4H_{10}$	2.5×10^{-19}	Table IIb
R12	$2C_2H_5 \xrightarrow{M} C_4H_{10}$	$2\ 9 \times 10^{-21}$	Table IIb
R13	$CH_2 + C_2H_2 \xrightarrow{M} CH_3C_2H$	$3\ 8 \times 10^{-25}$	Table IIb
R14	$H + C_2H_2 \xrightarrow{M} C_2H_3$	4.0×10^{-32}	Payne and Stief (1976)
R15	$H + C_2H_4 \xrightarrow{M} C_2H_5$	1.5×10^{-30}	Michael et al. (1973)
R16	$H + H \xrightarrow{M} H_2$	1.1×10^{-32}	Trainor et al. (1973)
R17	$CH_3C_2H + H \xrightarrow{M} C_3H_5$	4.4×10^{-31}	Whytock et al. (1976)
R18	$CH + H_2 \xrightarrow{M} CH_3$	1.7×10^{-28}	$1/10k_8$
R19	$CH_2 + H \xrightarrow{M} CH_3$	$1\ 7 \times 10^{-28}$	$1/10k_8$
R20	$C_3H_2 + H \xrightarrow{M} C_3H_3$	1.7×10^{-26}	$10k_8$
R21a	$C_3H_3 + H \xrightarrow{M} CH_3C_2H$	1.7×10^{-26}	$10k_8$
b	$\xrightarrow{M} CH_2CCH_2$	1.7×10^{-26}	$10k_8$
R22a	$^1CH_2 + C_2H_2 \xrightarrow{M} CH_3C_2H$	$3\ 8 \times 10^{-25}$	k_{13}
b	$\xrightarrow{M} CH_2CCH_2$	3.8×10^{-25}	k_{13}
R23	$CH_2 + C_2H_2 \xrightarrow{M} CH_2CCH_2$	3.8×10^{-25}	k_{13}
R24	$CH_3 + C_2H_3 \xrightarrow{M} C_3H_6$	1.3×10^{-22}	$10k_9$
R25	$2C_2H_3 \xrightarrow{M} 1,3\text{-}C_4H_6$	$1\ 3 \times 10^{-22}$	$10k_9$
R26	$C_2H_5 + C_2H_3 \xrightarrow{M} C_4H_8$	$1\ 3 \times 10^{-22}$	$10k_9$
R27a	$C_3H_3 + CH_3 \xrightarrow{M} 1,2\text{-}C_4H_6$	1.3×10^{-22}	$10k_9$
b	$\xrightarrow{M} 1\text{-}C_4H_6$	1.3×10^{-22}	$10k_9$
R28	$C_3H_5 + CH_3 \longrightarrow C_4H_8$	$1\ 3 \times 10^{-22}$	$10k_9$
R29	$CH_2CCH_2 + H \longrightarrow C_3H_5$	4.4×10^{-31}	k_{17}
R30	$C_3H_6 + H \xrightarrow{M} C_3H_7$	1.5×10^{-29}	$10k_{15}$

Notes. Extended set of three-body reactions of interest to the atmospheres of the outer solar system. The measured rate constants and those computed in Table IIb are used as basis for estimating the order of magnitude of other rate constants at 300°K (all units are in $cm^6\ sec^{-1}$).

to C_2H_3. The values of r for C_3H_3 and C_3H_5 with alkyl radicals are estimated in Table III.

As in the three-body combination reactions, utilization of the k_d/k_c ratios, when applied to the atmospheres of the outer planets, must be done with care. There is ample evidence to suggest the structure of transition states for disproportionation and for combination of alkyl radicals are not the same (Gibian and Corley, 1973). Therefore the combination reaction, which is a three-body reaction, would exhibit noticeable falloff in its rate at low pressure while the disproportionation process is expected to be pressure independent. At low pressures, therefore the importance of the disproportionation reaction will overwhelm that for

TABLE III

THE DISPROPORTIONATION AND THE COMBINATION RATE CONSTANT RATIO $r = k_d/k_c$ FOR IMPORTANT REACTIONS INVOLVING ALKYL AND VINYL RADICALS

	Reaction	r	Reference
R10	$CH_3 + C_2H_5$	0.04	Borrell and Platt (1970)
R11	$CH_3 + C_3H_7$	0.06	Terry and Futrell (1967)
R12	$C_2H_5 + C_2H_5$	0.13	LaLonde and Price (1971)
R25	$C_2H_3 + C_2H_3$	3.7	Christianson et al 1975; Takita et al 1968[a]
R24	$C_2H_3 + CH_3$	1	Estimated, this work[b]
R26	$C_2H_3 + C_2H_5$	1	Estimated, this work[b]
R28	$C_3H_5 + CH_3$	1	Estimated, this work

[a] Takita et al. (1968) deduced an approximate value of 3 for r. The value adopted here is from Christianson et al (1975)

[b] We assume that vinyl–alkyl reactions are intermediate in character between alkyl–alkyl and vinyl–vinyl reactions

combination and the k_d/k_c ratio will be significantly larger than that measured above the high-pressure limit.

CONCLUSION

We have identified a number of reactions of hydrocarbon radicals of importance in the planetary atmospheres of the outer solar system. For most of these reactions experimental data are not available. To model the atmospheres adequately the rate coefficients and their temperature dependence are required. We have been able to estimate the kinetic parameters for both abstraction and three-body combination reactions by use of several empirical and theoretical techniques. For abstraction reactions, the BSBL (bond strength–bond length) method in conjunction with transition state theory has been applied while for three-body combination reactions in the falloff region, the formalism of Troe has been used. Brief descriptions of the computational details and physical model required for successful estimation are described.

Yung has applied the kinetic parameters derived here along with other more accessible data, to an extensive model of the atmosphere of Titan. The results of the model calculations, when compared to observed specie concentration, are excellent and provide another example of synergism between direct observation of the planetary atmosphere, modeling, and laboratory chemical kinetics.

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