Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

CALCULATION OF THE THERMAL *A* FACTORS FOR METHYL AND ETHYL RUPTURE FROM CHEMICALLY ACTIVATED ETHYLTRIMETHYLSILANE. AN APPLICATION OF RRKM THEORY*

W. L. HASE AND J. W. SIMONS
Department of Chemistry, New Mexico State University, Las Cruces, New Mexico 88001 (U.S.A.)

(Received April 9th, 1971)

SUMMARY

The unimolecular decomposition of ethyltrimethylsilane, chemically activated by the insertion of a singlet methylene radical into a C–H bond of tetramethylsilane, has been studied from 0.03 to 70 mm Hg in the presence of oxygen. The singlet methylene radicals were produced by diazomethane photolysis at 4358 Å. Using neopentane and trimethylsilane as internal standards, the specific rate constant for ethyltrimethylsilane decomposition was determined to be 4.5×10^4 sec^{-1}. This rate correlates via RRKM theoretical calculations with thermal *A* factors in the range of $10^{14.8}$ to $10^{15.7}$ sec^{-1} for ethyl rupture and $10^{15.2}$ to $10^{16.4}$ sec^{-1} for methyl rupture from the Si atom of ethyltrimethylsilane. The range in these *A* factors reflects the uncertainties in the critical energies for these two paths.

INTRODUCTION

Evaluation of the *A* factors for Si–C bond breaking reactions is of considerable interest. In 1937 Helm and Mack[1] manometrically measured a first order *A* factor of $10^{15.2}$ sec^{-1} for tetramethylsilane decomposition. Recently, Davidson and Lambert[2] have studied the thermal decomposition of trimethylsilane and measured an *A* factor of $10^{16.1 \pm 0.5}$ sec^{-1} for Si–C bond rupture in trimethylsilane. In an earlier paper[3] we reported an *A* factor of $10^{15.0 \pm 0.5}$ sec^{-1} for Si–C bond cleavage in tetramethylsilane. These *A* factors are one to three orders of magnitude lower than those reported for C–C bond ruptures in alkanes[4].

In this paper we report *A* factors calculated for ethyl and methyl rupture from the Si atom of ethyltrimethylsilane. Chemically activated ethyltrimethylsilane was produced by the reaction of singlet methylene radicals with tetramethylsilane, and its decomposition rate was measured using an internal standard technique. The activated complex structures derived via RRKM theory calculations were used to calculate *A* factors for the two decomposition paths.

---

* The National Science Foundation is gratefully acknowledged for financial support.

RESULTS

Mixtures of diazomethane with tetramethylsilane (TMS) and either trimethylsilane or neopentane were photolyzed at 4358 Å. In the presence of oxygen the only significant reaction products were ethyltrimethylsilane, ethyldimethylsilane, and neohexane. The reactions were studied from 0.03 to 73 mm total pressure. The following reaction mechanism accounts for the observed products in the tetramethylsilane/trimethylsilane/diazomethane/oxygen system.

$$CH_2N_2 \xrightarrow{h\nu} {}^1CH_2 + N_2 \qquad (1)$$

$${}^1CH_2 + (CH_3)_4Si \xrightarrow{k_2} C_2H_5(CH_3)_3Si^* \qquad (2)$$

$$C_2H_5(CH_3)_3Si^* \xrightarrow{k_3} \text{Decomposition} \qquad (3)$$

$$\xrightarrow{w_4} C_2H_5(CH_3)_3Si \text{ (ETMS)} \qquad (4)$$

$${}^1CH_2 + (CH_3)_3SiH \xrightarrow{k_5} C_2H_5(CH_3)_2SiH^* \qquad (5)$$

$$C_2H_5(CH_3)_2SiH^* \xrightarrow{k_6} \text{Decomposition} \qquad (6)$$

$$\xrightarrow{w_7} C_2H_5(CH_3)_2SiH \text{ (EDMS)} \qquad (7)$$

When neopentane is added to the reaction mixtures instead of trimethylsilane the following reactions replace reactions (5)–(7):

$${}^1CH_2 + (CH_3)_4C \xrightarrow{k_8} C_2H_5(CH_3)_3C^* \qquad (8)$$

$$C_2H_5(CH_3)_3C^* \xrightarrow{k_9} \text{Decomposition} \qquad (9)$$

$$\xrightarrow{w_{10}} C_2H_5(CH_3)_3C \text{ (NEOH)} \qquad (10)$$

Only the reactions of singlet electronic state methylene radicals are considered here, since the added oxygen scavenges triplet methylene radicals and doublet radicals which are formed by decomposition of the excited species[5]. An asterisk denotes excess vibrational and internal rotational energy in the ground electronic state. The w's are collisional stabilization rate constants and, assuming unit collisional deactivation efficiency, are taken to be the appropriate gas kinetic theory collision frequencies of the excited molecules.

Application of the steady state approximation to reactions (1)–(10) leads to the following two equations.

$$\frac{[\text{EDMS}]}{[\text{ETMS}]}\cdot(1 + k_6/w_7) = k_5/k_2 + (k_5/k_2)\cdot(k_3/w_4) \qquad (11)$$

$$\frac{[\text{NEOH}]}{[\text{ETMS}]}\cdot(1 + k_9/w_{10}) = k_8/k_2 + (k_8/k_2)\cdot(k_3/w_4) \qquad (12)$$

where the product ratios have been normalized to a reactant ratio of 1. Plots of the left side of eqns. (11) and (12) *vs.* $1/w_4$ should be linear with k_3, the rate constant for ethyltrimethylsilane decomposition, equal to the slope divided by the intercept. The experimental values of k_6 and k_9 are 2.2×10^5 sec^{-1} and 4.6×10^5 sec^{-1}, respecively[3,6]. An experimental plot of values of $([\text{EDMS}]/[\text{ETMS}]) \cdot (1 + k_6/w_7)/(k_5/k_2)$ and $([\text{NEOH}]/[\text{ETMS}]) \cdot (1 + k_9/w_{10})/(k_8/k_2)$ *vs.* $1/w_4$ is given in Fig. 1. The values for k_5/k_2 and k_8/k_2 are 0.546 and 0.645, respectively. The solid line in Fig. 1 was determined by the method of least squares. The slope of the line is $k_3 = 4.5 \pm 0.6 \times 10^4$ sec^{-1}. The error quoted is the result using a 50% confidence limit. This rate constant is in good agreement with our previous[3] estimate of 3×10^4 sec^{-1}. A line drawn through the higher values in Fig. 1 would give a value for k_3 equal to 6.8×10^4 sec^{-1} and a line drawn through the lower values would give a value for k_3 equal to 3.2×10^4 sec^{-1}. These values are indicated by the dashed lines in Fig. 1.

DISCUSSION

Energetics

The average energy of the chemically activated ETMS is given by eqn. (13)

$$\langle E^* \rangle = -[\Delta H^0_{f_0}(\text{ETMS}) - \Delta H^0_{f_0}(\text{TEMS})] + [\Delta H^0_{f_0}(^1\text{CH}_2) + E^*(^1\text{CH}_2)] + E_{\text{th}} \qquad (13)$$

where $E^*(^1\text{CH}_2)$ is the excess energy carried by the singlet methylene radical from the photolysis reaction into the insertion product, ETMS*. A value for the quantity $\Delta H^0_{f_0}(^1\text{CH}_2) + E^*(^1\text{CH}_2)$ equal to 112.6 kcal/mole, as determined from *cis*-2-butene/diazomethane photolyses[7], was used since the "intrinsic reactivities" of *cis*-2-butene

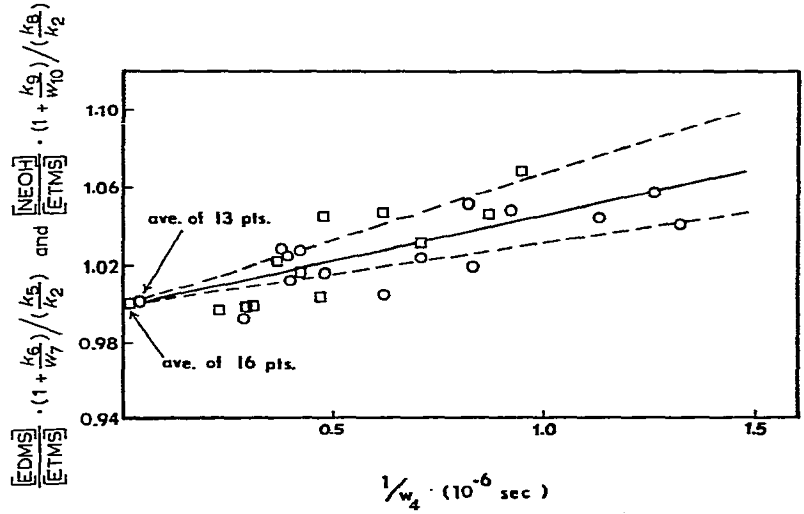

Fig. 1. Plot of $([\text{EDMS}]/[\text{ETMS}]) \cdot (1 + k_6/w_7)/(k_5/k_2)$, ○, and $([\text{NEOH}]/[\text{ETMS}]) \cdot (1 + k_9/w_{10})/(k_8/k_2)$, □, *vs.* $1/w_4$ (10^{-6} sec). The collision frequencies for each experimental point have been calculated with the following collision diameters; ETMS, 9.38 Å; EDMS, 8.18 Å; NEOH, 8.64 Å; trimethylsilane, 7.22 Å; TEMS, 8.64 Å; neopentane, 7.92 Å; CH_2N_2, 6.55 Å; and O_2, 4.55 Å[3,20]. The deactivation efficiency of O_2 was taken as 0.25 in accordance with the results of Kohlmaier and Rabinovitch[21].

and tetramethylsilane are nearly the same[8]. The average thermal energy, E_{th}, is 5.6 kcal/mole. There have been no experimental measurements of the difference in the heats of formation of ETMS and TEMS, but the difference can be determined quite accurately by the following procedure. The difference in the heats of formation of twenty related compounds, $\Delta H^0_{f_0}(C_2H_5X) - \Delta H^0_{f_0}(CH_3X)$, gave an average value of 3.5 ± 0.5 kcal/mole. The substituent group X varied from alkyl, alkenyl, and alkynyl to NH_2 and COOH. For the difference in the heats of formation of ETMS and TEMS the value, 3.4 kcal/mole, was used, which is the same as the difference in the heats of formation of neohexane and neopentane[9].

The critical energy for CH_3 rupture from the Si atom of ETMS was assumed to be 76 ± 2 kcal/mole, the same as for CH_3 rupture from TEMS[3]. For C_2H_5 rupture from ETMS the critical energy was assumed to be 3 kcal/mole lower than for methyl rupture, 73 ± 2 kcal/mole. This is the same difference as for ethyl and tertiary methyl rupture from neohexane[6].

Calculational procedure and activated complex models

The RRKM expression for k_{E^*}[10], the specific unimolecular dissociation rate constant at the energy E^*, is given by eqn. (14) where σ is the reaction path

$$k_{E^*} = \sigma \cdot \sum P(E^+_{vr}) / [h \cdot N^*(E^+ + E_0) \cdot F] \tag{14}$$

degeneracy, $\Sigma P(E^+_{vr})$ is the sum of vibrational-internal rotational states for the activated complex. $N^*(E^+ + E_0)$ is the density of the vibrational-internal rotational states for the molecule, and F is the centrifugal distortion factor. The sum and density terms for the molecule and activated complex were evaluated on an IBM-360 computer using the approximation of Whitten and Rabinovitch[11].

The vibrational frequencies for ETMS were assumed to be the same as for TEMS[12] with additional $-CH_2-$ vibrational modes chosen to be in agreement with frequencies for neohexane and neopentane[13]. The Si–C stretch for the ethyl group was assigned a frequency of 650 cm^{-1}. The vibrational frequency for the C–C–Si bend was assigned a value of 200 cm^{-1}. The C–C stretch was given the same frequency as the C–C stretch of the primary methyl group in neohexane. A complete description of the vibrational frequencies for ethyltrimethylsilane is given in Table 1. In the k_{E^*} calculations all internal rotations in the molecule were treated as free rotors since the excitation energy, E^*, is quite large, but in the thermal calculations the CH_3 torsion on the ethyl group was treated as a 201 cm^{-1} vibrator, the same as for neohexane[13]. The four internal rotations about the Si–C single bonds were treated as free rotors in the thermal calculations since the potential barriers to internal rotation about Si–C bonds are low[14].

Three different activated complex models were used for both ethyl and methyl rupture from the Si atom of ETMS. The reaction path corresponding to C–C bond rupture in ETMS was not included in the theoretical calculations since its contribution to the total reaction is negligible due to its large critical energy, ~84.0 kcal/mole, relative to the two other paths. The same rocking and bending motions were lowered in the activated complex for CH_3 rupture from the Si atom of ETMS as for CH_3 rupture from TEMS[3]. In the activated complexes for CH_3 rupture from the Si atom of ETMS the ethyl torsion and the three tertiary methyl torsions were treated as free rotors and the primary methyl torsion was treated as a 201 cm^{-1} vibrator. For ethyl

TABLE 1

VIBRATIONAL FREQUENCIES FOR ETHYLTRIMETHYLSILANE

Mode	ν (cm^{-1})	Mode	ν (cm^{-1})
C–H sym. stretch	2919(4)	C–H stretch	2940(2)
CH_2 sym. def.	1254	HCH bend	1450
Si–C skel. stretch	598, 696(2)	CH_2 wag	1200
C–H unsym. stretch	2963(2), 2967(6)	CH_2 twist	1150
CH_3 nonsym. def.	1430(8)	CH_2 rock	900
CH_3 rocking	869(8)	C–C skel stretch	1027
C–Si–C skel. def.	202(2), 239(3)	Si–C–C sekl. def.	200
CH_3 sym. def.	1253(3)	C–CH_3 torsion	201
Si–CH_3 torsion	Free rotor(3)	Si–C_2H_5 torsion	Free rotor
Si–C skel. stretch	650		

$E_z = 106.3$ kcal/mole.

rupture from ETMS, one CH_2 rock, one CH_2 twist, one C–C–Si bend and one C–Si–C bend were lowered in the activated complexes. All five torsions in the complexes for ethyl rupture from ETMS were treated as free rotors. The initial calculations were done at $E_0 = 73$ and 76 kcal/mole for ethyl and methyl rupture, respectively. The four adjustable frequencies in each of the two complexes for the two different decomposition paths were lowered by the same factor until the calculated and experimental overall decomposition rates were in agreement. The frequencies that give this agreement are given by Models IIM and IIE for methyl and ethyl rupture, respectively. This procedure assumes similar activated complex structures for both paths which seems reasonable since both processes are Si–C bond ruptures; *e.g.*, it has been found that the *A* factors for various carbon–carbon bond ruptures are all nearly identical[15]. Lowering the frequencies by the same factor for both reaction paths is also consistent with the calculations for neohexane decomposition[6], where the frequencies in the complex for ethyl rupture were lowered by a factor of 5.0 and the frequencies in the complex for tertiary methyl rupture were lowered by a factor of 5.3. The four adjustable frequencies for Models I and III were chosen so that they gave the same decomposition rates as Models IIM and IIE for methyl and ethyl rupture, respectively. The vibrational frequencies for the complex models are given in Table 2.

The calculational results using these complex models are given in Table 3. The *A* factors for ethyl rupture vary from $10^{14.8}$ to $10^{15.7}$ sec^{-1}. *A* factors calculated for methyl rupture vary from $10^{15.2}$ to $10^{16.4}$ sec^{-1} which are slightly larger than those calculated previously for methyl rupture from TEMS[3]. These *A* factors could be brought into better agreement by increasing the probability of ethyl rupture from ETMS *vs.* methyl rupture, but a significant increase above that already used does not seem very likely. If it is correct to assume that the frequencies in the activated complexes for methyl and ethyl rupture should be lowered by the same factors (the same following conclusions can be made if the factors differ by a small percentage) and if the rate constants determined here for ETMS are accurate to within a factor of two, then *A* factors calculated for CH_3 rupture from the Si atom of ETMS are in agreement only with the higher range of *A* factors calculated for TEMS decomposition, $10^{14.8}$ to $10^{15.6}$ sec^{-1}[3]. These higher *A* factors for TEMS were calculated using E^* values derived from the difference in the heats of formation of tetramethylsilane and tri-

TABLE 2

ACTIVATED COMPLEX MODELS FOR ETHYLTRIMETHYLSILANE DECOMPOSITION[a,b]

Ethyl rupture[c]

Motion	Molecule	Complex models		
		IE $E_0=71$[d]	IIE $E_0=73$	IIIE $E_0=75$
Si–C stretch	650	R.C.[e]	R.C.	R.C.
CH_2 twist	1150	540	418	324
CH_2 rock	900	422	327	253
C–Si–C bend	202	96	74	57
C–C–Si bend	200	94	73	56

Methyl rupture[f]

Motion	Molecule	Complex models		
		IM $E_0=74$	IIM $E_0=76$	IIIM $E_0=78$
Si–C stretch	696	R.C.	R.C.	R.C.
CH_3 rock	869(2)	416(2)	317(2)	245(2)
C–Si–C bend	239	115	87	67
C–Si–C bend	202	97	74	56

[a] A value of 1.6 was used for the partition function ratio for the adiabatic degrees of freedom for both ethyl and methyl rupture. This is the same value used for TEMS decomposition[6]. [b] All frequencies are in cm^{-1}. [c] The reaction path degeneracy is 1 for each complex. [d] E_0 is in kcal/mole. [e] R.C.=reaction co-ordinate. [f] The reaction path degeneracy is 3 for each complex.

TABLE 3

CALCULATIONAL RESULTS FOR ETHYLTRIMETHYLSILANE DECOMPOSITION[a]

Reaction	Model	E_0	k_{E^*}(sec^{-1}) $E^*=121.6$	A factor (sec^{-1})[b]
CH_3 Rupture	IM	74	1.50×10^4	1.63×10^{15}(15.2)
C_2H_5 Rupture	IE	71	3.00×10^4	6.31×10^{14}(14.8)
		Total k_{E^*}	4.50×10^4	
CH_3 Rupture	IIM	76	1.53×10^4	4.83×10^{15}(15.7)
C_2H_5 Rupture	IIE	73	2.99×10^4	1.72×10^{15}(15.2)
		Total k_{E^*}	4.52×10^4	
CH_3 Rupture	IIIM	78	1.51×10^4	2.82×10^{16}(16.4)
C_2H_5 Rupture	IIIE	75	3.01×10^4	4.80×10^{15}(15.7)
		Total k_{E^*}	4.52×10^4	
		Experimental	4.5×10^4	

[a] All energies are in kcal/mole. [b] The value of log A is in parentheses. The A factors were calculated for a temperature of 1000°K in accordance with the method of Glasstone *et al.*[19].

methylsilane as measured by Tannenbaum[16]. This result suggests that the correct value for the difference in heats of formation of tetra- and trimethylsilane is close to 9 kcal/mole, as measured by Tannenbaum. This difference is nearly the same as that found for the difference in the heats of formation of neopentane and isobutane at 298 °K, 7.5 kcal/mole. *A* factors calculated for methyl rupture from the Si atom of TEMS range from $10^{14.5}$ to $10^{15.2}$ sec^{-1} and $10^{14.4}$ to $10^{15.0}$ sec^{-1} using E^* values derived from the measurements of Davidson *et al.*[17] (13.0 kcal/mole) and Potzinger and Lampe[18] (15.0 kcal/mole), respectively, for the difference in the heats of tetramethylsilane and trimethylsilane[3]. *A* factors calculated for CH_3 rupture from the Si atom of ETMS would be in agreement with these *A* factors for CH_3 rupture from TEMS if the experimental rate constant determined here for ETMS decomposition is too high by the rather large factor of ~ 10. It should be noted that an *A* factor in the range of $10^{15.2}-10^{16.4}$ sec^{-1} for methyl rupture from the Si atom of ETMS is in agreement with the *A* factor, $10^{16.1\pm0.5}$ sec^{-1}, measured by Davidson and Lambert[2] for methyl rupture from trimethylsilane.

These calculated *A* factors for tetramethylsilane and ethyltrimethylsilane as well as the *A* factors measured for tetramethylsilane[1] and trimethylsilane[2] decomposition indicate that the entropy of activation for Si–C bond rupture is much lower than that for C–C bond rupture. Using the value of $10^{17.4}$ sec^{-1} for the neopentane *A* factor [4,8] and $10^{15.6}$ sec^{-1} for the tetramethylsilane *A* factor, both at 1000 °K, the entropies of activation for the two processes are 16.6 e.u. and 8.4 e.u., respectively. This result indicates that neopentane and tetramethylsilane decompose via activated complexes having similar vibrational and internal rotational entropies, and since the entropy of tetramethylsilane is larger than that for neopentane the entropy of activation for tetramethylsilane decomposition is smaller. It will be interesting to see if this trend of smaller *A* factors continues for the rest of the Group IV tetramethyls.

EXPERIMENTAL

The apparatus employed was the same as previously described[3]. Matheson lecture-bottle neopentane was purified by gas chromatography and analyses showed it to be free of impurities. NMR specialties tetramethylsilane, 99.9% pure, was used without further purification. Trimethylsilane was prepared *in vacuo* by the reaction of trimethylchlorosilane with $LiAlH_4$ in dibutyl ether and was purified by gas chromatography. Diazomethane was prepared by the reaction of *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide with a saturated solution of KOH in 1,4-butanediol and was stored in di-n-butyl phthalate at liquid nitrogen temperature.

The reactant mixtures were photolyzed for times varying from 2 h at high pressures and up to 30 h at the lower pressures. All reactions were carried out to less than 5% conversion of the silane and alkane substrates. There were no measurable products formed from dark reactions, and no products of interest were formed from CH_2N_2/O_2 photolyses.

The analyses of the products condensable at −196°K were done by gas–liquid phase chromatography. The analytical column used consisted of 25 feet of 30% dibutyl phthalate on chromosorb and 4 feet of didecyl phthalate on Chromosorb. Mixtures nearly identical to the reaction mixtures were used to calibrate the column for the measured products.

REFERENCES

1 D. F. HELM AND E. MACK, JR., *J. Amer. Chem. Soc.*, 59 (1937) 60.
2 I. M. T. DAVIDSON AND C. A. LAMBERT, *J. Chem. Soc. D*, (1969) 1276.
3 W. L. HASE AND J. W. SIMONS, *J. Chem. Phys.*, 52 (1970) 4004; W. L. HASE, Ph.D. Thesis.
4 H. M. FREY AND R. WALSH, *Chem. Rev.*, 69 (1969) 103; R. L. JOHNSON, W. L. HASE AND J. W. SIMONS, *J. Chem. Phys.*, 52 (1970) 3911.
5 See refs. 2–9 in ref. 3 above; P. S. LEE, R. L. RUSSELL AND F. S. ROWLAND, *J. Chem. Soc. D*, (1970) 18.
6 W. L. HASE, R. L. JOHNSON AND J. W. SIMONS, *Int. J. Chem. Kinet.*, in press.
7 J. W. SIMONS AND G. W. TAYLOR, *J. Phys. Chem.*, 73 (1969) 1274; G. W. TAYLOR AND J. W. SIMONS, *J. Phys. Chem.*, 74 (1970) 464.
8 W. L. HASE AND J. W. SIMONS, *J. Chem. Phys.*, 54 (1971) 1277.
9 *American Petroleum Institute Research Project*, No. 44, Carnegie Institute of Technology, Pittsburg, Pa., 1944–1952.
10 R. A. MARCUS, *J. Chem. Phys.*, 43 (1965) 2658; E. V. WAAGE AND B. S. RABINOVITCH, *Chem. Rev.*, 70 (1970) 377; E. V. WAAGE AND B. S. RABINOVITCH, *J. Chem. Phys.*, 52 (1970) 558.
11 G. Z. WHITTEN AND B. S. RABINOVITCH, *J. Chem. Phys.*, 38 (1963) 2466; G. Z. WHITTEN AND B. S. RABINOVITCH, *J. Chem. Phys.*, 41 (1964) 1883; D. C. TARDY, B. S. RABINOVITCH AND G. Z. WHITTEN, *J. Chem. Phys.*, 48 (1968) 1427.
12 K. SHIMIZU AND H. MURATO, *J. Mol. Spectrosc.*, 5 (1960) 44.
13 R. G. SNYDER AND J. H. SCHACHTSCHNEIDER, *Spectrochim. Acta*, 21 (1965) 169.
14 J. R. DURIG, S. M. CRAVEN AND J. BRAGIN, *J. Chem. Phys.*, 52 (1970) 2046; 53 (1970) 38.
15 WING TSANG, *Int. J. Chem. Kinet.*, 1 (1969) 245.
16 S. TANNENBAUM, *J. Amer. Chem. Soc.*, 76 (1954) 1027.
17 S. J. BAND, I. M. T. DAVIDSON AND C. A. LAMBERT, *J. Chem. Soc. A*, (1968) 2068.
18 P. POTZINGER AND F. W. LAMPE, *J. Phys. Chem.*, 74 (1970) 719.
19 S. GLASSTONE, K. J. LAIDLER AND H. EYRING, *The Theory of Rate Processes*, McGraw-Hill, New York, 1941.
20 S. C. CHAN, B. S. RABINOVITCH, J. T. BRYANT, L. D. SPICER, T. FUJIMOTO, Y. N. LIN AND S. P. PAVLOU *J. Phys. Chem.*, 74 (1970) 3160.
21 G. H. KOHLMAIER AND B. S. RABINOVITCH, *J. Chem. Phys.*, 38 (1963) 1709.