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Catalytic Effect of CO_2 and H_2O Molecules on $^{\bullet}CH_3 + {}^3O_2$ Reaction

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Abstract: The methyl ($^{\bullet}CH_3$) + $^3O_2$ radical is an important reaction in both atmospheric and combustion processes. We investigated potential energy surfaces for the effect of CO_2 and H_2O molecules on a $^{\bullet}CH_3$+ O_2 system. The mechanism for three reaction systems, i.e., for $^{\bullet}CH_3 + {}^3O_2$, $^{\bullet}CH_3 + {}^3O_2$ (+CO_2) and $^{\bullet}CH_3 + {}^3O_2$ (+H_2O), were explored using *ab initio*/DFT methods [CCSD(T)//M062X/6-311++G(3df,3pd)] in combination with a Rice−Ramsperger−Kassel−Marcus (RRKM)/master-equation (ME) simulation between a temperature range of 500 to 1500 K and a pressure range of 0.0001 to 10 atm. When a CO_2 and H_2O molecule is introduced in a $^{\bullet}CH_3 + {}^3O_2$ reaction, the reactive complexes, intermediates, transition states and post complexes become thermodynamically more favorable. The calculated rate constant for the $^{\bullet}CH_3 + {}^3O_2$ (3×10^{-15} cm^3 molecule^{-1} s^{-1} at 1000 K) is in good agreement with the previously reported experimentally measured values (~1×10^{-15} cm^3 molecule^{-1} s^{-1} at 1000 K). The rate constant for the effect of CO_2 (3×10^{-16} cm^3 molecule^{-1} s^{-1} at 1000 K) and H_2O (2×10^{-17} cm^3 molecule^{-1} s^{-1} at 1000 K) is at least one–two-order magnitude smaller than the free reaction (3×10^{-15} cm^3 molecule^{-1} s^{-1} at 1000 K). The effect of CO_2 and H_2O on $^{\bullet}CH_3 + {}^3O_2$ shows non-RRKM behavior, however, the effect on $^{\bullet}CH_3 + {}^3O_2$ shows RRKM behavior. Our results also demonstrate that a single CO_2 and H_2O molecule has the potential to accelerate a gas-phase reaction at temperature higher than >1300 K and slow the reaction at a lower temperature. The result is unique and observed for the first time.

Keywords: $^{\bullet}CH_3$ radical; $^3O_2$ radical; water and CO_2 catalysis; *ab initio*/DFT; RRKM/ME

Table S1. Redundant internal coordinates of reactants, complexes, products and transition states obtained using M06-2X/6-311++G(3df,3pd) taken from gaussian checkpoint file.

(a) CH_3 + O2==> CH_2O + HO								
CH_3	**O2**	**RC**	**TS1**	**Int-1**	**TS2**	**Int-2**	**TS3**	**PC**
Charge = 0 Multiplicity = 2 C,0,0.,0.0000001111,0. H,0,0.,1.0777366481,0. H,0,0.9333472196,-0.5388681574,0. H,0,-0.9333472196,-0.5388681574,0.	Charge = 0 Multiplicity = 3 O,0,0.,0.,0.5938390313 O,0,0.,0.,-0.5938390313	Charge = 0 Multiplicity = 2 C,0,1.8997714092,-0.0664721368,0.0062984681 H,0,2.8506584729,0.4285997927,-0.1067299613 H,0,1.4618940515,-0.1790384676,0.9847565221 H,0,1.4299904275,-0.5347288055,-0.8430811359 O,0,-1.1963623159,-0.5340216705,0.0181992062 O,0,-0.9340330452,0.6235922877,-0.0317200992	Charge = 0 Multiplicity = 2 C,0,1.4339638582,-0.2046069761,-0.0410368641 H,0,1.2214213268,-0.8590570237,-0.8695753476 H,0,1.9830981651,0.7036117787,-0.2253348697 H,0,1.4263302762,-0.6132038152,0.9553642996 O,0,-1.4487802232,-0.2232333464,0.0680200964 O,0,-0.5966254034,0.6278073826,0.0554966854	Charge = 0 Multiplicity = 2 C,0,1.0834664449,-0.1804472322,-0.0001082544 H,0,1.8656879945,0.5739675178,-0.0013639845 H,0,1.1289955479,-0.7984400885,-0.8947011964 H,0,1.1299548664,-0.7964391472,0.8958223944 O,0,-0.1586125223,0.5374362406,-0.0002462856 O,0,-1.1639032867,-0.2759242567,0.0004183265	Charge = 0 Multiplicity = 2 C,0,0.9388590949,-0.2544999682,0.0000010222 H,0,-0.0646701964,-1.1176538946,-0.0000088906 H,0,1.4752222341,-0.3712422543,0.9384606463 H,0,1.4752292384,-0.3712280823,-0.9384563723 O,0,-0.0226634543,0.7318364354,0.0000048771 O,0,-1.0432839167,-0.3075832363,-0.0000051994	Charge = 0 Multiplicity = 2 C,0,-1.1182753679,0.2495177688,0.1009269949 O,0,-0.0616592219,-0.5721750027,-0.1043478323 H,0,-2.0482595693,-0.2983885706,0.0873675153 H,0,-1.0289521776,1.2622953239,-0.2662874842 O,0,1.1285915628,0.1897888208,-0.0986381492 H,0,1.4024397739,0.1249366599,0.8254409554	Charge = 0 Multiplicity = 2 O,0,-1.1459127775,0.2668963639,0.1515185491 O,0,0.1140577578,-0.5656744801,-0.0691365158 C,0,1.1500525939,0.2192667703,-0.0246249871 H,0,-1.7068948891,-0.1333909624,-0.5241121322 H,0,1.9409175785,-0.0386007085,0.6680410743 H,0,1.1244157364,1.1542780168,-0.5687379885	Charge = 0 Multiplicity = 2 C,0,1.5777780365,0.2822699021,-0.0015875695 H,0,2.6478461523,0.0256072139,0.0282689007 H,0,1.3014230777,1.3485055912,-0.0235890276 O,0,-1.3195911422,1.3914153616,-0.0823238318 O,0,0.7359114379,-0.5727025142,-0.0099451524 H,0,-0.8940748015,0.5112897552,-0.0613047294
(b) CH_3 + O2 (+CO2) ==> CH_2O + HO + (CO2)								
RC-c	**TS-1c**	**Int-1c**	**TS2-c**	**Int-2c**	**TS3-c**	**PC-c**		
Redundant internal coordinates	Charge = 0	Charge = 0 Multiplicity = 2	Charge = 0 Multiplicity = 2	Charge = 0	Charge = 0 Multiplicity = 2	Charge = 0 Multiplicity = 2 Redundant internal coordinates found in file.		

found in file.
C,0,-0.4030909032,2.1732845739,-0.039004478
H,0,-1.0333168495,1.8447244599,-0.8479346676
H,0,0.5094972709,2.7025562777,-0.2567075994
H,0,-0.7649253611,2.1310466408,0.9739071184
O,0,-2.0535206436,-0.8989835335,-0.2932914930
O,0,-1.3454265749,-0.6556317048,0.6289091873
O,0,1.7416644438,-0.1157549469,0.9595284092
C,0,1.4080898453,-0.3073376273,-0.1282295770
O,0,1.0862937724,-0.5106441398,-1.2181028998

Multiplicity = 2

Redundant internal coordinates found in file.
C,0,-2.1875741635,1.111516921,-0.1127930915
H,0,-3.2431327932,0.9080762668,-0.1801929581
H,0,-1.6884885065,1.5872492361,-0.9396438474
H,0,-1.7276724197,1.160195513,0.8602016983
O,0,-1.4992373669,-0.9750645377,-0.5322306612
O,0,-0.5484529229,-1.3215940059,0.1194040508
O,0,0.9720302583,1.1865989513,-0.3834934449
C,0,1.6791471910,0.3711023634,0.0279173060
O,0,2.3960747255,-

C,0,1.8972499291,0.8673673169,0.0003322581
H,0,2.9275540525,1.2119081956,0.0004787045
H,0,1.3654431143,1.1912976433,0.8922755081
H,0,1.3652010269,1.1926737843,-0.8909565106
O,0,1.9684108625,-0.5670933699,-0.0007915275
O,0,0.7916878482,-1.1002205451,-0.0007398964
O,0,-1.1408640631,1.2541227984,-0.0019952162
C,0,-1.6318247677,0.2070525461,-0.0000731203
O,0,-2.1499450027,-0.8214343697,0.0018638002

C,0,-1.8218639969,0.6102913195,-0.1937577276
H,0,-1.5838656751,0.1672093957,1.0305690043
H,0,-2.8918080842,0.5359797015,-0.3691190218
H,0,-1.3172358151,-1.5675651673,-0.2915408757
O,0,-1.0904268012,-0.4745186353,-0.6340879938
O,0,-0.9213294928,-0.8846977384,0.7552183638
O,0,1.0878711434,1.2799329222,0.2120133097
C,0,1.4912389222,0.2198283069,-0.0156601843
O,0,1.9224927998,-0.8231494394,-0.2423418746

Multiplicity = 2

Redundant internal coordinates found in file.
C,0,-1.0887458618,1.1574292376,0.5420865617
O,0,-1.1456866272,0.3542998278,-0.5481397390
O,0,-1.7517108906,-0.8711694851,-0.1952247472
C,0,1.5033962303,-0.1961386946,0.0287415513
O,0,1.9319617688,0.8206219602,-0.2966152538
O,0,1.0958019026,-1.2288459137,0.3576874373
H,0,-0.9856437682,-1.3935614119,0.0852516491
H,0,-0.6501881541,2.1147658758,0.3037901544
H,0,-1.8573735999,1.0249206217,1.2894423862

Redundant internal coordinates found in file.
C,1.9747406962,-1.0181701747,0.1950561680
O,0,1.0162594944,-0.2616934525,-0.2391772591
O,0,1.4869366434,1.205982271,-0.2438445785
C,0,-1.6723657435,-0.0277295638,0.0684029918
O,0,-1.9115433862,-1.1403255187,-0.1014790728
O,0,-1.4609130758,1.0961900654,0.2455305054
H,0,0.6543041902,1.6166283116,0.0286598833
H,0,2.2902178716,-1.8389637241,-0.4351852921
H,0,2.5077063096,-0.7315752145

C,0,-1.9136499046,-1.2889220091,0.0434040673
O,0,-0.7884085292,-0.9502256698,-0.1923419416
O,0,-1.7958978164,1.602610716,0.0063607139
C,0,1.6847928571,0.1520348181,0.0242313927
O,0,2.1763938999,-0.8620026965,0.2528363251
O,0,1.2220663057,1.1887000368,-0.2018108232
H,0,-0.8335671716,1.4705206777,-0.0600651658
H,0,-2.3247115401,-2.2243122859,-0.366464402
H,0,-2.5763443219,-0.6788132984,0.6745011392

	0.432572708,0.438304948				2,1.091450654	
(c) CH_3 + O2 (+H2O) ==> CH_2O + HO + (H2O)						
RC-h	**TS1-h**	**Int-1h**	**TS2-h**	**Int-2h**	**TS3-h**	**PC-h**
Charge = 0 Multiplicity = 2 C,0,-2.9636513464,-0.3835134796,0.06668426 07 H,0,-2.8446201901,-0.008445291 4,1.0703247 H,0,-3.0409003528,-1.444490263 4,-0.106457842 7 H,0,-3.0719173659,0.3059045 698,-0.754674328 4 O,0,-0.2121025312,-0.0830678856,-0.216687471 7 O,0,0.0709524791,1.0285247424,0.0 974197551 O,0,2.8563003458,-0.4376879687,0.0193938 134 H,0,2.4922548209,0.445	Charge = 0 Multiplicity = 2 Redundant internal coordinates found in file.	Charge = 0 Multiplicity = 2 C,0,1.989789814,0.7875366116,-0.0811574753 H,0,3.0504302885,0.9628979976,-0.234411247 H,0,1.6269250 35,1.2549502159,0.8318943371 H,0,1.3944598435,1.1233628274,-0.927674082 O,0,1.8499740534,-0.6403203797,0.0440870018 O,0,0.6211565482,-0.9873213832,0.2324612046 O,0,-0.8539093498,1.5141204285,0.2373504368 H,0,-0.5807852007,0.5888125413,0.2718150823 H,0,-1.803676031	Charge = 0 Multiplicity = 2 C,0,0.8683996768,0.9160541372,-0.2974059457 H,0,0.8270586272,-0.1175822586,-1.1228867987 H,0,1.8496426871,1.3750771343,-0.3833947123 H,0,-0.0369759716,1.4852749183,-0.4911940252 O,0,0.7536002182,-0.0074138808,0.7243472696 O,0,0.6907288555,-1.0641203717,-0.2770759835 H,0,-2.0196278109,0.0784147994,-0.0502692443	Charge = 0 Multiplicity = 2 C,0,-1.2046444252,1.3464885854,0.4278112487 O,0,-1.3834583052,0.4214636796,-0.5368260622 O,0,-1.3700780893,-0.8703227592,0.0330891711 H,0,-0.4081566356,-1.0397149008,0.0737981063 H,0,-1.2958843618,2.3506376926,0.0400368336 H,0,-1.5175474983,1.0784058796,1.4276364445 O,0,1.3431802731,-0.4157034045,0.0995154707 H,0,1.6204537091,-0.2916733247,-	Charge = 0 Multiplicity = 2 C,0,1.8231543739,-0.9650389761,0.1093036112 O,0,0.9886689498,-0.2674098783,-0.5885269449 O,0,1.2941423622,1.2471427378,-0.3784731755 H,0,0.3920130 57,1.5225281222,-0.1380817114 H,0,2.4522674208,-1.6765580972,-0.4134786567 H,0,1.9705569916,-0.7203629676,1.1543839736 O,0,-1.4770561095,1.0348928162,0.0246392083 H,0,-1.179911592	Charge = 0 Multiplicity = 2 C,0,-1.6122629331,-1.3436095392,-0.084820079 O,0,-0.5210833955,-1.7446048934,-0.3934505332 O,0,-1.2972870327,1.981907949,0.4491861397 H,0,-0.4053931507,1.5682205643,0.3794271931 H,0,-2.4877381609,-2.0091141187,-0.1377457547 H,0,-1.7694562693,-0.3081356201,0.2539383693 O,0,1.0008741071,0.5056466964,0.1820751427 H,0,1.7096625242,0.7367278558,-0.4195391864 H,0,0.6725663109,-0.3650698941,-0.0952382916

4042496,0.103558306 H,0,2.09732 71408,-1.000170673 ,-0.1445961925	07,-2.1604009753 H,0,-2.9427920692,-0.6708449302,-1.8614498144 H,0,-4.0667475657,-0.7414961254,-2.8916341757	9,1.5133581406,0.3647767418	H,0,-1.4592927479,-0.6416866639,-0.3556078892 H,0,-1.7201795344,0.2119361858,0.8522753293	0.8113213768 H,0,1.0597363328,0.4587305521,0.3947391642	6,0.1697894282,-0.2763009244 H,0,-2.0461914531,1.3680348147,-0.6717123802	

Table S2. Rotational -vibrational parameters obtained from vibrational analysis.

	Int-1	**Int-2**	**TS2**	**TS3**	**PC**	**RC**	**TS1**
	146.53	213.15	-1852.31	-540.95	159.5	68.69	-335.06
	523.15	323.73	273.88	253.54	216.51	131.16	78.2
	978.2	519.98	777.59	432.04	221.23	141.98	225.5
	1151.17	706.47	913.57	481.86	443.92	227	486.76
	1204.56	962.11	1046.05	638.91	595.72	327.61	506.26
	1311.29	1190.62	1114.31	1172.8	1230.77	517.35	797.08
	1462.75	1233.29	1154.6	1196.02	1289.01	1417.06	1421.23
	1474.73	1423.45	1180.84	1296.6	1539.28	1421.94	1422.54
	1485.2	1456.33	1467.94	1490.13	1851.53	1765.77	1586.67
	3050.05	3151.17	2017.66	3116.27	2995.26	3120.34	3122.15
	3160.59	3294.63	3078.21	3253.22	3087.37	3302.3	3297.67
	3161.14	3818.26	3203.36	3852.9	3671.35	3309.78	3301.61
D1	53.65327	54.40369	36.00364	52.97019	40.59308	38.69067	48.3499
2D1	11.60987	11.54995	14.84479	10.85359	5.47897	5.39689	7.11037
2D2	10.16483	9.91932	11.349	9.47676	4.8274	4.89403	6.47351
2D	10.86335	10.70363	12.97974	10.14184	5.142877	5.139313	6.784471

		with CO2				
RC-c	**Int-1-c**	**Int-2-c**	**TS1-c**	**TS2-c**	**TS3-c**	**PC-c**
27.95	12.79	75.03	-291.63	-1844.62	-627.36	25.51
52.82	83.03	110.7	15.11	72.36	42.88	45.08
71.61	107.98	146.48	66.4	117.1	64.36	94.2
99.95	125.31	173.98	78.29	142.98	97.94	108.99
111.57	134.58	199.5	89.1	168.93	133.03	121.98
127.25	151.76	315.53	111.47	176	155.77	128.46
150.06	526.43	399.25	119.84	316.72	365.34	172.15
179.66	687.58	525.46	232.53	696.08	442.71	175.47
202.4	702.13	691.09	427.18	698.43	478.82	364.7
250.59	975.5	696.02	475.84	777.55	687.11	411.41

531.08	1154.23	701.67	694.95	910.21	694.92	698.69	
	686.37	1200.55	970.51	702.63	1042.85	700.58	703.03
	697.88	1322.51	1196.7	794.26	1113.67	1186.31	1229.34
	1414.55	1417.03	1236.32	1416.82	1147.11	1207.27	1289.92
	1415.77	1465.2	1413.99	1417.84	1187.77	1314.95	1418.51
	1426.25	1472.42	1455.78	1424.43	1416.48	1414.76	1546.03
	1767.56	1475.77	1462.8	1589.54	1470.13	1497.88	1861.88
	2458.21	2465.06	2461.46	2461.49	2023.03	2459.9	2467.16
	3114.85	3055.35	3156.52	3126.3	2464.59	3134.36	2989.42
	3292.37	3160.27	3301.51	3297.35	3086.37	3272.15	3079.76
	3312.79	3176.67	3788.22	3318.45	3216.31	3814.91	3752.09
D1	3.73527	6.67195	5.79898	5.16278	6.34068	5.75165	4.19245
2D1	2.18941	1.9743	2.41654	1.90179	2.42273	2.09119	1.98536
2D2	1.8719	1.53835	1.88351	1.4514	2.01829	1.57801	1.36603
2D	2.02444	1.742746	2.133443	1.661402	2.211283	1.816568	1.646834

with H2O

RC-h	Int-1-h	Int-2-h	TS1-h	TS2-h	TS3-h	PC-h	TS1-ah
33.92	114.43	124.97	-227.12	-1839.1	-691.5	56.71	-278.56
59.76	132.05	162.9	48.36	156.55	31.87	75.33	63.95
73.21	166.51	205.83	66.06	198.82	138.93	170.76	97.58
109.86	178.3	249.08	88.52	216.08	191.97	224.59	120.29
134.85	203.37	303.05	146.96	220.5	220.82	248.06	140.16
164.89	382.37	346.5	178.02	342.15	247.57	249.89	182.43
175.12	489.12	507.03	199.25	359.32	386.1	262.18	218.12
184.83	536.05	535.51	240.38	501.38	459.18	412.52	234.3
226.4	965.85	737.68	270.79	775.2	504.84	508.03	283.32
258.87	1139.77	762.49	412.13	909.39	601.01	638.97	481.41
268.31	1206.89	969.48	480.23	1051.29	722.12	807.99	499.02
504.29	1337.45	1201.04	768.86	1120.01	1183.16	1245.2	807.96
1405.35	1462.73	1256.09	1416.21	1143.6	1233.84	1292.85	1417.94
1416.58	1474.34	1457.36	1421.91	1192.91	1361.56	1552.15	1421.39
1634.52	1480.23	1532.87	1598.78	1460.92	1499.37	1641.2	1583.59
1748.11	1636.03	1631.89	1644.11	1655.85	1623.61	1844.98	1626.49
3113.78	3052.37	3141.51	3119.56	2017.39	3105.54	2993.4	3130.46
3293.15	3163.39	3283.58	3300.78	3094.13	3241.9	3099.79	3306.55
3306.85	3172.02	3579.23	3312.63	3228.06	3690.38	3481.74	3316.6
3899.57	3787.86	3817.19	3896.65	3869.68	3859.92	3682.82	3885.76
3997.12	3961.99	3948.9	3988.122	3955.5	3971.45	3966.72	3985.35
18.10487	11.34254	10.20971	17.97533	11.00459	13.22988	6.98875	7.81707
1.82558	4.08591	4.60744	2.1712	4.45225	3.54628	3.32137	3.27206

1.68733	3.06194	3.57528	1.96377	3.79697	3.00099	2.26552	2.43621
1.755094	3.537063	4.058681	2.064882	4.111576	3.262262	2.743106	2.823371

Table S3. Calculated equilibrium constants (K_{eq} in cm^3 $molecule^{-1}$) for the formation of two-body and three body complexes.

Temp	RC	Ke-1-c	Ke-2-c	Ke-1-h	Ke-2h
500	8.48E-16	9.11E-25	2.85E-27	2.07E-26	7.11E-23
600	5.09E-18	9.88E-25	3.02E-27	2.33E-26	5.29E-23
700	1.34E-19	1.11E-24	3.37E-27	2.68E-26	4.59E-23
800	8.95E-21	1.27E-24	3.86E-27	3.10E-26	4.35E-23
900	1.11E-21	1.46E-24	4.47E-27	3.60E-26	4.35E-23
1000	2.13E-22	1.68E-24	5.19E-27	4.16E-26	4.50E-23
1100	5.60E-23	1.92E-24	6.03E-27	4.79E-26	4.75E-23
1200	1.87E-23	2.19E-24	6.98E-27	5.49E-26	5.09E-23
1300	7.48E-24	2.49E-24	8.06E-27	6.25E-26	5.49E-23
1400	3.45E-24	2.82E-24	9.26E-27	7.09E-26	5.97E-23
1500	1.78E-24	3.18E-24	1.06E-26	8.00E-26	6.50E-23

Details of chemical kinetics analysis

For pressure-dependent reactions, Rice−Ramsperger−Kassel−Marcus (RRKM)/master equation (ME) was used and the energy-dependent specific unimolecular rate constants ki(E, J) is given by [39]

$$k(E) = L^{\neq}\frac{1}{h}\frac{G^{\neq}(E-E_0)}{\rho(E)} \quad \text{(S1)}$$

where $L^{\neq} = \frac{m^{\neq}}{m}\times\frac{\sigma_{ext}}{\sigma_{ext}^{\neq}}$ is the reaction path degeneracy; $\sigma_{ext}^{\neq}$ and σ_{ext} are the external rotation symmetry numbers of the transition state and reactant; $m^{\neq}$ and m are the numbers of optical isomers (mirror image) of the transition state and reactant, respectively, h is Planck's constant; is the density of states of the reactant molecule; $G^{\neq}(E-E_0)$ is the sum-of-states of the transition state; , E_0 is the reaction threshold energy, and ϱ(E) is the density of states of the reactant molecule. The sums and densities of states were computed using DenSum as implemented in MultiWell Program. The internal energy E is measured relative to the zero point energy of the reactant molecule and the reaction threshold energy (critical energy) is the difference between the zero point energies of reactant and transition state. The pressure-dependent rate constants were simulated using estimated energy transfer parameters for the intermediates. The tunnelling corrections were implemented based on asymmetric Eckart potential. The approximated temperature-dependent exponential down <ΔE>down = 200 *(T/ 300)0.85 cm^{-1} [28,32] was used to calculate the rate constants. The Lennard-Jones parameters for collider gases (N_2) εk_B, $\sigma(N_2)$ = 3.74 Å, ε/kB(N2) = 82 K were used in our calculation based on previous studies.[28,32] The bimolecular rate constant describing collisions between N2 and the complex , intermediate ("Well") was based on Lennard-Jones collisions with net parameters obtained using the usual combining rules from parameters for the two collision partners: N2 gas (σ = 3.74 Å and ε/kB = 82 K)52 and the Well (σ = 5.20 Å and ε/kB = 212 K, used for all Wells).The double arrays used in MultiWell for the master equation simulations consisted of 5000 array elements with 10 cm−1 energy grains, with the quasi-continuum regime evaluated up to 50000 cm−1 . At each temperature and pressure, master equation simulations were initiated using the chemical activation energy distribution, which is appropriate for recombination reactions.

The calculated rate constants in the high-pressure limit (k_∞) were fit to the modified Arrhenius expression $k_\infty^{bimol}(T) = A \times T^n(Exp - (\frac{Ea}{RT}))$ in the temperature range of 500 – 1500 K.