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THE KINETICS OF THE THERMAL DEGRADATION OF CALCIUM CARBONATE*

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The decomposition of calcium carbonate fine powder in a flowing nitrogen atmosphere has been investigated by non-isothermal thermogravimetry at heating rates in the range, 10–50 deg $\min^{-1}$. The analog percentage weight change record was digitized at 1 deg intervals. The resulting data, transformed into dimensionless extents of reaction and calculated rates of reaction, was then subjected to the Arrhenius, Friedman and Generalized Kissinger analyses, using a recently developed FORTRAN program system. The value of n namely 0.39 ± 0.04, resulting when the data is analyzed assuming an nth order reaction, strongly indicates that the most probable rate controlling step is a three-dimensional diffusion process (D4 mechanism), with $E = 172.4$ kJ$\cdot$mol^{-1} and $A = 1.97 \cdot 10^4$ K$^{-1} \cdot$min^{-1}. Reasons for the wide disparity in previously reported kinetic data are discussed.

The ever-increasing impact of the acid rain problem has emphasized even more the need to develop efficient procedures for in situ removal of sulfur dioxide, produced from high sulfur coals in large combustion systems. Atmospheric Fluidized Bed Combustion (AFBC) utilizes naturally occuring limestone or dolomite admixed with the fossil fuel as feedstock. Calcination proceeds and theoretically the sulfur dioxide produced in the combustion zone is removed by lime absorption prior to stack emission. Flue Gas Desulfurization (FGD) may entail the use of calcined limestone physically separated from the burning fuel. The efficiency of either gettering process will be governed by the nature of the calcium sulfate (or sulfite) formation reaction. This may well be similar to the calcium carbonate formation process, which in turn may be analogous to the reverse dissociation reaction. An understanding of the nature of these reactions is considered to be of

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prime importance. This paper is concerned with the findings of a study of the calcination reaction.

The thermal degradation of calcite has been the subject of intensive study over the years [1]. Beruto and Searcy [2] find that most activation energy values (E) reported prior to 1974 are close to the enthalpy of degradation, 178 $\mathrm{kJ \cdot mol^{-1}}$ (see ref. 733 in the Brown, Dollimore and Galwey review) [1]. At this time, Zsakó and Arz [3] analyzed previously reported experimental data from three sources. They employed the nth order function $(1-\alpha)^n$, to represent $f(\alpha)$ in the general rate Eq. (1). For degradative studies carried out in an air atmosphere, E values ranging from 110–742 $\mathrm{kJ \cdot mol^{-1}}$, and pre-exponential factors, A, varying between $1.6 \cdot 10^2$–$3.2 \cdot 10^{33}$ $\mathrm{min^{-1}}$, were obtained. When data obtained under various partial pressure carbon dioxide atmospheres was analyzed, even greater values were obtained; namely, $E = 709$–1558 $\mathrm{kJ \cdot mol^{-1}}$, $A = 1.6 \cdot 10^{32}$–$7.9 \cdot 10^{68}$ $\mathrm{min^{-1}}$. It is true, as Zsakó and Arz state, that the investigative conditions do influence the results. However, we strongly disagree with these authors who state that the great differences in the kinetic parameter values obtained are in no way related to the calculation procedures.

It is the purpose of this paper to show how non-isothermal thermogravimetry at medium heating rates, in the range 10–50 $\mathrm{deg \cdot min^{-1}}$ can be used to study the calcination reaction, to derive the kinetic parameters for a reasonably mechanism, and to show why the calculation techniques are all important.

Experimental

All non-isothermal thermogravimetric measurements (NITG) were carried out in 100 $\mathrm{ml \cdot min^{-1}}$ flowing 99.9% pure nitrogen in the Perkin–Elmer TGS–2/System 4 analyzer with the $X-Y_1-Y_2$ recorder, employing the previously-described [4] temperature control procedure. Analytical reagent-grade calcium carbonate (Mallinckrodt #4072) was used at a sample size 3.7–3.8 mg. In order that the weight loss was recorded over 100% of the recorder chart width, a 56% weight suppression was applied, and the data recorded in the percent initial weight mode. This analog data, amplified 100 ×, was digitized at 1 °C intervals and transferred to magnetic tape. This information was then transferred off-line to the in-house computer for analysis by programs TGDATCON/TGKIN as has been described [5, 6].

Results

Figure 1 shows the percentage weight-loss data from 550–850 °C at six heating rates from 10–50 °C $\cdot$ min^{-1}. Program TGDATCON [5] employs a cubic spline interpolation to generate the rates of weight loss (DTG) from the 301 NITG digitized data values. In performing this interpolation, one may select any cubic spline interval (CSI), which need not necessarily be the smallest, namely unity. Both large (CSI = 20) and small (CSI $\leq$ 5) intervals have been used. The resulting pertinent maximum reaction rate data, together with the analog T(max) and DTG (max) signal values, is summarized in Table 1. Although the use of the larger interval results in smoother DTG data, as exemplified by the lower number of "spikes" (cf. columns 5 and 11), the smaller interval data is considered more accurate. As previously indicated [5], at low heating rates, $\leq$ 10 °C $\cdot$ min^{-1}, it is expected that the analog and calculated T (max) and DTG (max) will agree within the limits of experimental error. This is the case for the low CSI data. At β = 10 °C $\cdot$ min^{-1}, the analog values are 735 °C and 0.23 mg $\cdot$ min^{-1}, as compared with calculated values of 736 °C and 0.238 mg $\cdot$ min^{-1}. Using the 20° CSI, although the maximum temperatures agree, the calculated DTG (max) is 0.256 mg $\cdot$ min^{-1}, which is significantly greater than the analog value. For this reason, all kinetic analyses were carried out on the low CSI transposed data. The increasing difference between the analog and calculated T(max) and DTG (max) values with increase in heating rate is expected, and has been explained [5]. The DTG curves shown in Fig. 1 are the initial run data at each heating rate. These curves exhibit characteristic features typical of both a two dimensional phase boundary shrinkage ($R2$ mechanism) or three dimensional diffusion ($D4$ mechanism) as the rate-controlling step in the thermal degradation [7].

The total transposed TG/DTG data, in the form $1-\alpha$ and $d\alpha/dt$, has been subjected to a computerized kinetic analysis, using program TGKIN [6]. For comparison, four kinetic models, namely, F, n (nth order); $R2$ (contracting cylinder); $D2$ and $D4$ (two and three dimensional diffusion), have been employed, and Arrhenius, Friedman and Generalized Kissinger [8] analyses performed. The results are summarized in Table 2. All analyses performed were based upon the solid-state reaction rate law (1).

$$d\alpha/dt = A.\ T.\exp(-E/RT)\cdot f(\alpha) \tag{1}$$

In performing the Arrhenius analyses, the entire data from 0.1% to 99% extent of reaction was able to be used. If one assumes the most simple model, namely a first-order reaction, the kinetic parameters obtained are of the same order of magnitude as those given by Zsakó and Arz [3]. The E and A values tend to decrease slightly with increase in heating rate from 10 to 50 °C $\cdot$ min^{-1}. The value of α corresponding

Table 1 Calcium carbonate thermal degradation maximum reaction rate data

Analog			Calculated low C.S.I.						Calculated high C.S.I.					
β, °C·min^{-1}	T, °C	dw/dt mg·min^{-1}	CSI °C	SP*	T, °C,	dw/dt, mg·min^{-1}	α	dα/dt, min^{-1}	CSI °C	SP*,	T, °C	dw/dt, mg·min^{-1}	α	dα/dt, min^{-1}
10	~735	~0.23	5	15	736	0.238	0.7621	0.1412	20	2	735	0.256	0.7535	0.1518
			5	15	734	0.242	0.7283	0.1440	20	4	735	0.264	0.7484	0.1573
15	~755	~0.34	2	55	755	0.357	0.7667	0.2134	20	2	755	0.369	0.7720	0.2203
			2	44	754	0.350	0.7596	0.2077	20	2	754	0.367	0.7644	0.2174
20	~767	~0.40	5	22	767	0.424	0.7602	0.2504	20	3	768	0.420	0.7726	0.2480
			5	19	765	0.435	0.7718	0.2585	10	6	768	0.434	0.8101	0.2576
25	~778	~0.48	3	38	777	0.520	0.7890	0.3119	20	2	774	0.544	0.7544	0.3264
			5	20	779	0.507	0.7710	0.3036	20	3	775	0.525	0.7278	0.3144
40	~802	~0.74	5	18	801	0.794	0.7807	0.4688	20	2	796	0.812	0.7258	0.4793
			5	20	798	0.769	0.7705	0.4532	20	3	795	0.809	0.7401	0.4764
50	~815	~0.86	3	37	813	0.936	0.7821	0.5739	20	4	812	0.956	0.7716	0.5863
			5	18	812	0.932	0.7818	0.5647	20	2	812	0.955	0.7824	0.5788

* Number of spikes in calculated DTG record.

Table 2 Calcium carbonate thermal degradation summary of kinetic analyses

	Model F, n		Model $D4$	Model $D2$	Model $R2$
Arrhenius	$n = 1$	$n = 0.39 \pm 0.04$			
$0.01 < \alpha < 0.990$					
E (kJ·mol^{-1})	256.1–246.1	196.1–176.5	466.9 446.1	443.0 427.6	203.5–190.0
A (K·min)$^{-1}$	(10.0–1.59)·10^9	(33.3- 2.79)·10^5	(713–5.78)·10^{17}	(143–3.28)·10^{17}	(59.5–7.48)·10^5
C.C.	0.967–0.981	0.981-0.992	0.989 0.995	0.984 0.992	0.983–0.993
Kissinger					
$10 < \beta < 50$					
E (kJ·mol^{-1})		167.7	172.4	172.0	166.5
A (K·min)$^{-1}$		1.05·10^5	1.97·10^4	8.27·10^4	4.46·10^4
C.C.		>0.999	>0.999	>0.999	>0.999
Friedman					
$0.1 < \alpha < 0.6$					
E (kJ·mol^{-1})		166.9 ± 5.6	172.0 ± 3.6	172.0 ± 3.6	172.0 ± 3.6
A (K·min)$^{-1}$		$1.20 \pm 0.08 \cdot 10^5$	$1.53 \pm 0.67 \cdot 10^4$	$6.29 \pm 2.56 \cdot 10^4$	$1.03 \pm 0.36 \cdot 10^5$
C.C.		$\geqslant 0.99$	$\geqslant 0.99$	$\geqslant 0.99$	$\geqslant 0.99$

to the DTG (max), see Table 2, indicates [8] a much lower value of n, namely, 0.39. Using this order, the much lower kinetic parameter values shown were obtained. It should be noted that the linear regressions are much more successful when the correct n-value is used, as indicated by the higher correlation coefficients. This value of n is higher than that corresponding to a $D2$ mechanistic model, ($f(\alpha) = [-\ln(1-\alpha)]^{-1}$); namely, 0.27. It is lower than that corresponding to either a $D4$ model, ($f(\alpha) = 1.5[(1-\alpha)^{-1/3}-1]$); namely, 0.43 or an $R2$ mechanism, ($f(\alpha) = 2(1-\alpha)^{1/2}$); namely, 0.5. Therefore, the data was analyzed assuming each of these models, as shown in Table 2. As can be seen, the Arrhenius energies of activation and pre-exponential factors are disparate, a not unexpected result in view of the recent findings [7].

When the maximum reaction rate and temperature data in Table 1 is subjected to the Generalized Kissinger analyses, more rational behavior prevails, as can be seen in Table 2. Indeed, irrespective of the model selected, the E values are very close to the pre-1974 values surveyed by Beruto and Searcy [2].

The data has also been subjected to Friedman analyses; namely, Arrhenius analyses at constant extents of reaction. Over the range, $0.1 < \alpha < 0.6$, fairly consistent kinetic parameter values result, as shown in Table 2. The mean values are in good agreement with the Kissinger values.

As is obvious from the foregoing, great care has to be taken in interpreting kinetic parameters resulting from the Arrhenius analysis employing the basic rate Eq. (1). Consider the experimental data, curve A in Fig. 1. The peak value of α, 0.7621 (see Table 1), corresponds to $n = 0.412$. Part of the transposed TG/DTG data is listed in Table 3, columns 2–3. The Arrhenius analysis parameters, $\ln[(\mathrm{d}\alpha/\mathrm{d}t)/(f(\alpha)\cdot T)]$ for the $D4$ and F, n (0.412) models, and $1/T$, are also given, columns 4–6. At 685°, it is easily calculated that $f(\alpha) = 16.9241$ and 0.9004 for the $D4$ and F, n models, respectively. As can be seen, the logarithmic parameters are very different, resulting in the two distinct sets of E and A values! However, purely as empirical parameters of the simple Eq. (1), both are correct.

Discussion

Arnold et al. [9] have discussed the nth order Arrhenius model, [$f(\alpha) = (1-\alpha)^n$ in Eq. (1)], purely from a mathematical point of view. They concluded that, as a means of estimating the kinetic parameters, the equation is badly conditioned, but that it is a well-fitting empirical model. Furthermore, they state a wide range of parameter triplet values (E, A, n), may be obtained from a single TG curve. This, indeed, is the case here, as can be seen by comparing the two sets of F, n model results in Table 2. If both the heating rate, β, and the order of the reaction, n, are held constant, as

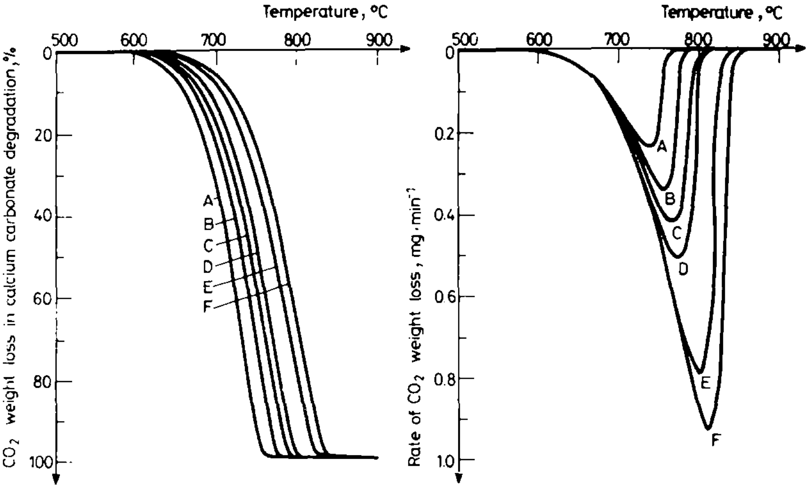

Fig. 1 Calcium carbonate degradation TG/DTG Data *A*, 10; *B*, 15; *C*, 20; *D*, 25; *E*, 40; *F*, 50 deg·min^{-1}

Arnold and his co-workers state, it is difficult to see how one can have the long and narrow confidence domains in a log $A-E$ plot for a unique TG curve which they indicate. There is no doubt that such a domain exists. However, the experimental data recorded in duplicate for six different heating rates in this investigation indicates that, within the narrow range of n values calculated from the α_{max} values, the kinetic parameter doublets (E, A) lie within a much less extended domain; namely, E, ln A from 196.1, 15.02 to 176.5, 12.54.

Theoretically, the $f(\alpha)$ dependency of the Arrhenius equation is removed in the Friedman and Generalized Kissinger equations [10]. This is borne out in practice when they are used in the analysis of experimental data, as evidenced in Table 2. It is considered that these are realistic values for the energy of activation and pre-exponential factors for the thermal degradation of calcium carbonate. The question is, since the data fits each of the three models so well, which is correct?

Arnold et al. [9] in discussing the possible rate-controlling steps in thermal decompositions of the solid to solid and gas type, indicate that heat transfer should not be discounted. Using high-pressure molded, 1 cm diameter, 90% theoretical density calcium carbonate spheres, Hills [11] has in fact demonstrated that with these exceedingly large, ~1.5 gram sized samples, both heat and mass transfer are all important. With regard to the very small particle size and sample size used in this study, it is considered that temperature gradients are so small as to be neglected. Hills, furthermore, offers evidence to show that the slow mass transfer step is the removal of carbon dioxide by diffusion from a spherical calcium carbonate-oxide interface moving towards the center of the sphere. As Brown, Dollimore and Galwey

Table 3 Calcium carbonate thermal degradation Arrhenius analysis, $\beta = 10\ ^\circ\mathrm{C}\cdot\mathrm{min}^{-1}$, run #1

			$\ln[(d\alpha/dt)/(f(\alpha)\cdot T)]$		
T, °C	$1-\alpha$	$d\alpha/dt\cdot 10^3$, min^{-1}	$D4$	F, 0.412	$10^4/T$, K^{-1}
590	0.9960	3.11	−19.555	−12.530	11.585
610	0.9869	7.41	−17.518	−11.682	11.323
620	0.9789	9.68	−16.781	−11.423	11.196
635	0.9588	15.91	−15.618	−10.935	11.011
645	0.9398	22.19	−14.903	−10.605	10.891
655	0.9147	29.70	−14.256	−10.313	10.774
675	0.8333	52.59	−12.975	− 9.725	10.547
685	0.7751	65.52	−12.419	− 9.485	10.437
695	0.7038	75.54	−11.950	− 9.314	10.329
710	0.5643	104.60	−11.114	− 8.913	10.171
715	0.5090	113.71	−10.852	− 8.792	10.120
720	0.4508	121.29	−10.606	− 8.682	10.069
725	0.3876	130.05	−10.341	− 8.555	10.019
730	0.3213	135.61	−10.091	− 8.441	9.969
735	0.2520	140.77	− 9.821	− 8.309	9.919
740	0.1817	138.67	− 9.569	− 8.194	9.870
745	0.1145	129.87	− 9.315	− 8.074	9.822
750	0.0532	112.96	− 9.011	− 7.903	9.774
755*	0.0100	44.81	− 9.154	− 8.143	9.726
765*	0.0040	3.53	−11.328	−10.316	9.633
E ($\mathrm{kJ}\cdot\mathrm{mol}^{-1}$)			469.51	195.78	
A ($\mathrm{K}\cdot\mathrm{min})^{-1}$			$1.308\cdot 10^{20}$	$3.333\cdot 10^{6}$	
C.C.			0.9941	0.9902	

* Excluded from regression

[1] point out, this is a generally prevailing view. Beruto and Searcy [2] conclude that, without rapid removal of carbon dioxide from the moving interface, the dissociation equilibrium can be established. Since calcium oxide is approximately 10% more dense than the carbonate, diffusion of the carbon dioxide through the thickening lime shell may become progressively slower. Any temperature gradient across the grain will progressively increase throughout the non-isothermal scan, and thus will not favor any reformation of carbonate.

Of the three models considered in the kinetic analyses of the experimental data, the $D4$ mechanism, namely three dimensional diffusion control according to Ginstling–Brounshtein [12], is most favored. The mean experimental α_{max} value, 0.39 ± 0.4, is closest to the theoretical value, 0.43. In calculating this value, the necessary algorithms do not take into account the Carter modification, [13] which incorporates the product to reactant molar volume ratio into the integral form of the $f(\alpha)$ dependency. In the case of calcium carbonate degradation, this ratio is 0.5

and may well have a not insignificant effect on the magnitudes of the various α-parameters used in the analyses (see Table 1, Ref. 6). However, it is considered that a more important factor controlling the rate of removal of carbon dioxide from the shrinking interface is the pore structure of the continually produced calcium oxide. This structure is very probably highly dependent on the heating rate employed.

To emphasize this point further, Fig. 2 shows NITG weight gain curves at 50 deg·min^{-1} characterizing the formation of calcium carbonate from three lime sources. As can be seen, only the in situ produced lime shows any significant carbon dioxide absorptive activity, curve C. This curve does exhibit classic features; an initial reaction, an induction period followed by an accelerating region which merges into a short-lived steady rate region. Presumably the continually-produced calcium carbonate acts increasingly as a barrier to its further formation. Thus, only 29% of the theoretical weight gain was achieved. This data, while quite inconclusive, does make one obvious point. The formation of calcium carbonate by lime absorption of carbon dioxide, and very possibly calcium sulfate by lime absorption of sulfur trioxide, cannot be studied by NITG at this fast heating rate. Isothermal thermogravimetry will have to be used with in situ produced lime.

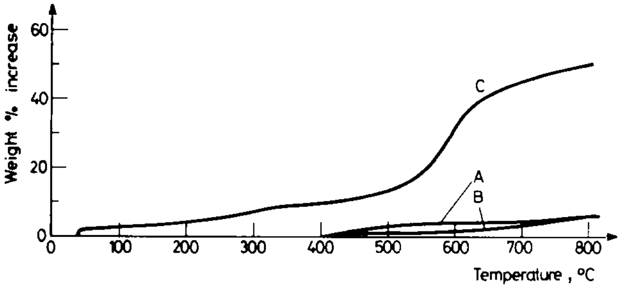

Fig. 2 Calcium carbonate formation NITG data at 50 deg·min^{-1}. A: as-received reagent grade calcium oxide fine powder. B: material *A* previously heated at 50 deg·min^{-1} in nitrogen to 900 °C. C: material produced by thermall degrading calcium carbonate in nitrogen at 50 deg·min^{-1} and cooled to ambient temperature

Conclusions

Non-isothermal thermogravimetry has been used successfully to investigate the thermal degradation of very small particle-size calcium carbonate. Even though experimental procedures should never be discounted, kinetic analysis calculation techniques are of primary importance in contradiction of the Zsakó and Arz statement [3]. We are in complete agreement with the caveat of Arnold et al. [9]

concerning the interpretation of Arrhenius analysis E and A parameter values. However, it is considered that such analyses have more utility than just a means of calculating empirical parameter values for curve-fitting purposes. When carried out at fixed extents of reaction, the results are very consistent and in good agreement with those obtained by Generalized Kissinger analysis. As has been pointed out (see Ref. 1, p. 89), the calculated energies of activation are relatively insensitive to the form of $f(\alpha)$ in Eq. (1). For the F, n model, the correct value of the reaction order, n, must be used.

In the early stages of the decomposition, phase boundary contraction in the calcite ($R2$ mechanism), may well be the slow step in the overall process. However, as the reaction proceeds, it is considered that the slow diffusion of carbon dioxide from the shrinking interface ($D4$ mechanism), becomes rate-determining, with $E = 172.4\ \mathrm{kJ \cdot mol^{-1}}$ and $A = 1.97 \cdot 10^4\ \mathrm{K^{-1} \cdot min^{-1}}$.

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Zusammenfassung — Die Zersetzung von feinpulvrigem Calciumcarbonat im Stickstoffstrom wurde durch nicht-isotherme Thermogravimetrie bei Aufheizgeschwindigkeiten von 10–50 °C/min untersucht. Die analoge prozentuale Gewichtsverlustregistrierung wurde in Intervallen von einem Grad digitalisiert. Die erhaltenen, in solche eines dimensionslosen Reaktionsgrades überführten Daten und berechnete Reaktionsgeschwindigkeiten wurden der Arrhenius-, der Friedmann- und einer verallgemeinerten Kissinger-Analyse unterzogen, wobei ein kürzlich aufgestelltes FORTRAN-Programm benutzt wurde. Der unter der Annahme einer Reaktion n-ter Ordnung für n erhaltene Wert von 0.39 ± 0.04 ist ein nachdrücklicher Hinweis darauf, daß der geschwindigkeitsbestimmende Schritt höchstwahrscheinlich ein dreidimensionaler Diffusionsprozeß ($D4$-Mechanismus) mit $E = 172.4\,\mathrm{kJ\cdot mol^{-1}}$ und $A = 1.97\cdot 10^4\,\mathrm{K^{-1}\cdot min^{-1}}$ ist. Gründe für die weitreichende Verschiedenheit der bisher mitgeteilten kinetischen Daten werden diskutirt.

Резюме Разложение порошкообразного карбоната кальция было исследовано неизотермической термогравиметрией в потоке азота при скоростях нагрева 10–50° в минуту. Процент изменения веса, снимаемый в виде аналогового сигнала, был превращен в цифровую форму с интервалом в 1°. Конечные данные, преобразованные в безразмерные степени реакции и вычисленные скорости реакции, были затем, используя недавно разработанную программу фортран, представлены в уравнения Аррениуса, Фридмана и обобщенное уравнение Киссинджера. Когда данные анализировались в предположении n-порядка реакции, значение $n = 0{,}39 \pm 0{,}04$ показало, что наиболее вероятной стадий контролирующей скорость, является трехразмерный диффузионный процесс (Д4 механизм) с $E = 172{,}4$ кдж·моль$^{-1}$ и $A = 1{,}97\cdot 10^4$ К$^{-1}$·мин$^{-1}$. Обсуждены причины большого несоответствия ранее приведенных кинетических данных.