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KINETICS OF THE THERMAL DECOMPOSITION OF HYDROGEN PEROXIDE VAPOR¹

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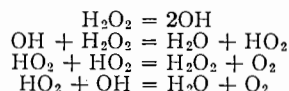
ABSTRACT

The rates of thermal decomposition of hydrogen peroxide vapor were measured by the static method at low pressures (0.2 to 20 mm. Hg), over the temperature range 300°–600° C., in carefully cleaned glass vessels. The reaction was of the first order with respect to time and the final products were only water and oxygen. Around 400° C. the character of the reaction changed gradually from heterogeneous (surface effects, low activation energy) to homogeneous (reproducible rates in various vessels). With initial pressures of about 10 mm. Hg the experimental rates above 400° lead to an apparent activation energy of 43 kcal. and a frequency factor of $10^{10.7}$. After correction for the residual surface decomposition, the rate equation becomes

$$k = 10^{13} \exp(-48,000/RT) \text{ sec.}^{-1}$$

in good agreement with the accepted value for the O—O bond dissociation energy. The reaction rates increased regularly with pressure.

Packing the reaction vessels with glass rods and adding various gases (including nitric oxide and propylene) had no appreciable effect on the gas-phase reaction. Deuterium peroxide vapor decomposed at the same rate as hydrogen peroxide under comparable conditions. The results may be explained adequately by the following non-chain mechanism for the uncatalyzed decomposition:



INTRODUCTION

One of the very first chemical reactions of which the rate was measured was the spontaneous decomposition of hydrogen peroxide (Thenard, 1818). Yet, in spite of countless investigations, our understanding of this deceptively simple reaction is still far from adequate. Obviously the major difficulty here comes from the extreme sensitivity of hydrogen peroxide to all sorts of catalysts. In recent years two independent investigators (15, 24) have shown that under suitable conditions, such as in a flow system, the homogeneous decomposition becomes measurable at temperatures somewhat above 400° C. Because of the uncertainty in analyzing the data in a flow experiment we felt that a study by the static method, if successful, would yield more reliable results, particularly for the activation energy. In fact we were able to follow the reaction at temperatures appreciably higher than heretofore (up to 600° C.) and it was possible to evaluate with good accuracy the relative importance of the surface and volume reactions.

EXPERIMENTAL

The reaction vessels, generally 2-liter flasks, were either of Pyrex or Vycor. First they were cleaned thoroughly with hot fuming sulphuric acid and, after they were rinsed,

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they were either fused in a blast lamp as described before (8), or treated for a few hours with hot, concentrated hydrogen peroxide. Even after such treatments the Pyrex flasks required some preliminary runs (a dozen or so) before yielding reproducible results. Vycor flasks, on the contrary, gave immediately consistent results. In addition they could be used safely above 500° C.

The reaction vessels were heated in a heavily insulated electric furnace (Fig. 1) the temperature of which was controlled to within $\pm 0.3^\circ$ and read to $\pm 0.7^\circ$ by means of

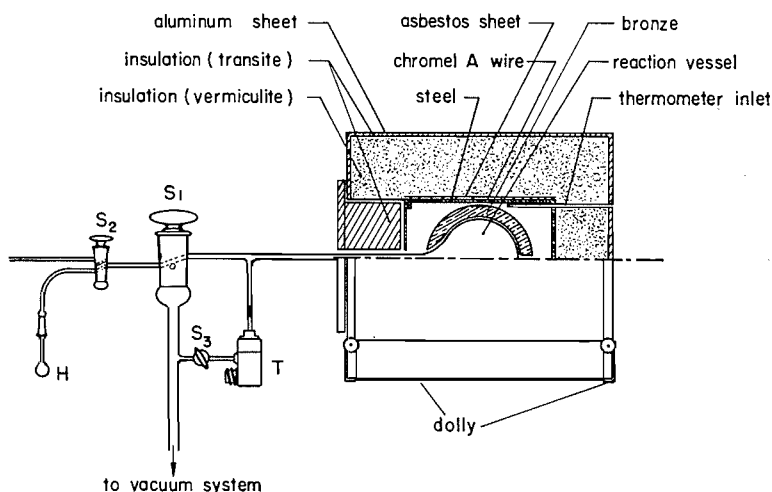


FIG. 1. Apparatus used to follow the thermal decomposition of hydrogen peroxide vapor.

an electronic thermometer. The sensitive element of the latter (platinum coil on quartz) was calibrated against a certified platinum resistance thermometer (Leeds and Northrup) up to 470° C. Beyond that range a large-scale, well adjusted extrapolation gave an accuracy estimated at 1.5° or better. Temperature gradients inside the furnace were minimized by enclosing the glass flasks within thick hemispheres of aluminum bronze. Aluminum foil provided good thermal contact between the flask and the metal shell. The thermometer bulb was inserted directly in a slot in one of the hemispheres.

A large three-way stopcock S_1 , lubricated with silicone grease, connected the reaction chamber either with the vacuum system or with the reagents. The rate of the reaction was followed by recording the pressure increase with a pressure transducer T . The characteristics of these devices and their use in the present investigation have been described elsewhere (10). At first glass spoon-gauges coupled to a linear transducer were used; later this fragile combination was replaced by the all-metal transducers with identical results. The dead volume of the reaction system outside the furnace was only of the order of 50 cc.; these parts were kept at 90° C. to prevent condensation of the vapor. Tests confirmed that the decomposition of the peroxide vapor in the dead space was negligible. The reaction vessel was filled by evaporation of the sample of liquid peroxide kept in a small bulb H at 70°–80° C. Because of the low volatility of hydrogen peroxide the maximum pressure obtainable in a reasonable time by that technique was not higher than 20 mm. Hg. Higher pressures require boilers of special construction (21).

To study the effect of various added gases on the reaction rate an auxiliary reservoir was needed for mixing the reagents. To that end a 5-liter flask, kept at about 150° C.

in a heating mantle, was connected to the reaction system. The peroxide vapor was first introduced, as described above, then the other gas at a given partial pressure, from a storage vessel fitted with a second pressure transducer. The peroxide vapor mixed with the various gases used did not react measurably at 150° in the storage vessel. The preparation of the hydrogen peroxide samples 99.9% pure from Becco's 90% product has been described before. The deuterium peroxide, about 95%, was obtained by fractional distillation of the product from dissociation of heavy water in the electrical discharge (11). The various gases, presumably 98–99% pure, were taken directly from cylinders without further purification. Good reproducibility was achieved only by following rigorously the same experimental procedure. For instance, the reaction chamber had to be evacuated for the same length of time between runs (20 to 30 minutes depending on the temperature) and the initial pressure of reactants had to be constant in any given series. The experiments were scattered with respect to temperature to minimize any aging of the glass surface, albeit no sign of this ever appeared.

RESULTS

The majority of the some 700 runs carried out were in the temperature range 400°–500° C. and at initial pressures of 8 to 10 mm. Hg where the reproducibility was generally good (Fig. 2). As a rule consecutive runs yielded the same rate constant within the accuracy of measurements; non-consecutive runs with a given vessel generally agreed within 10 or 15%. All the runs (save a few in coated vessels) gave time–pressure curves strictly of the first order. Little attention was paid to the heterogeneous decomposition in the region below 400° C. as it has been studied extensively before (for a review cf. (22)). Its sole importance in this investigation was to provide a basis for correcting the rates at higher temperatures for any residual surface reaction. The apparent activation energy for this process was rather low, 10–12 kcal. as found before. The rates, however, were at least 30 times slower (for instance $k = 3 \times 10^{-4}$ sec.⁻¹ at 350° C.) than the slowest ones obtained previously under comparable conditions (8). As a consequence the transition temperature from heterogeneous to homogeneous decomposition was lowered to about 400° (Fig. 3).

In one series of runs the surface was increased by packing the reaction vessel with Pyrex tubes 8 mm. in diameter sealed at both ends under reduced pressure, and arranged as evenly as possible in space inside the flask. Increase in the surface-to-volume ratio from 0.4 to 0.7 and 1.1 cm.⁻¹ produced only a slight increase in the reaction rate above 400–425° C. but a more substantial rate increase of the heterogeneous reaction (Fig. 3). Likewise addition of various gases (air, oxygen, argon, and helium) had only minor effects on the rate as may be judged from Table I. In general an increase in total pressure accelerated the reaction slightly, the various gases being comparable in that respect. The curves of Fig. 4 illustrate the dependence of the reaction rate on the total initial pressure. The levelling off at low pressures is undoubtedly the result of increasing importance of the surface reaction. This is confirmed by the accompanying drop in apparent activation energy, down to 38 kcal. at 0.3 mm. Hg. The low-pressure limit at which the decomposition could be followed with the type of transducer used (Statham Laboratories, Model P97–0.05d) was of the order of 0.2 mm. Hg. The reaction was then slowed down enough to enable measurements up to 600° C. ($k = 2.5 \times 10^{-2}$ sec.⁻¹) in a 2-liter Vycor vessel.

Nitric oxide and propylene, commonly used as a test for free radicals in organic re-

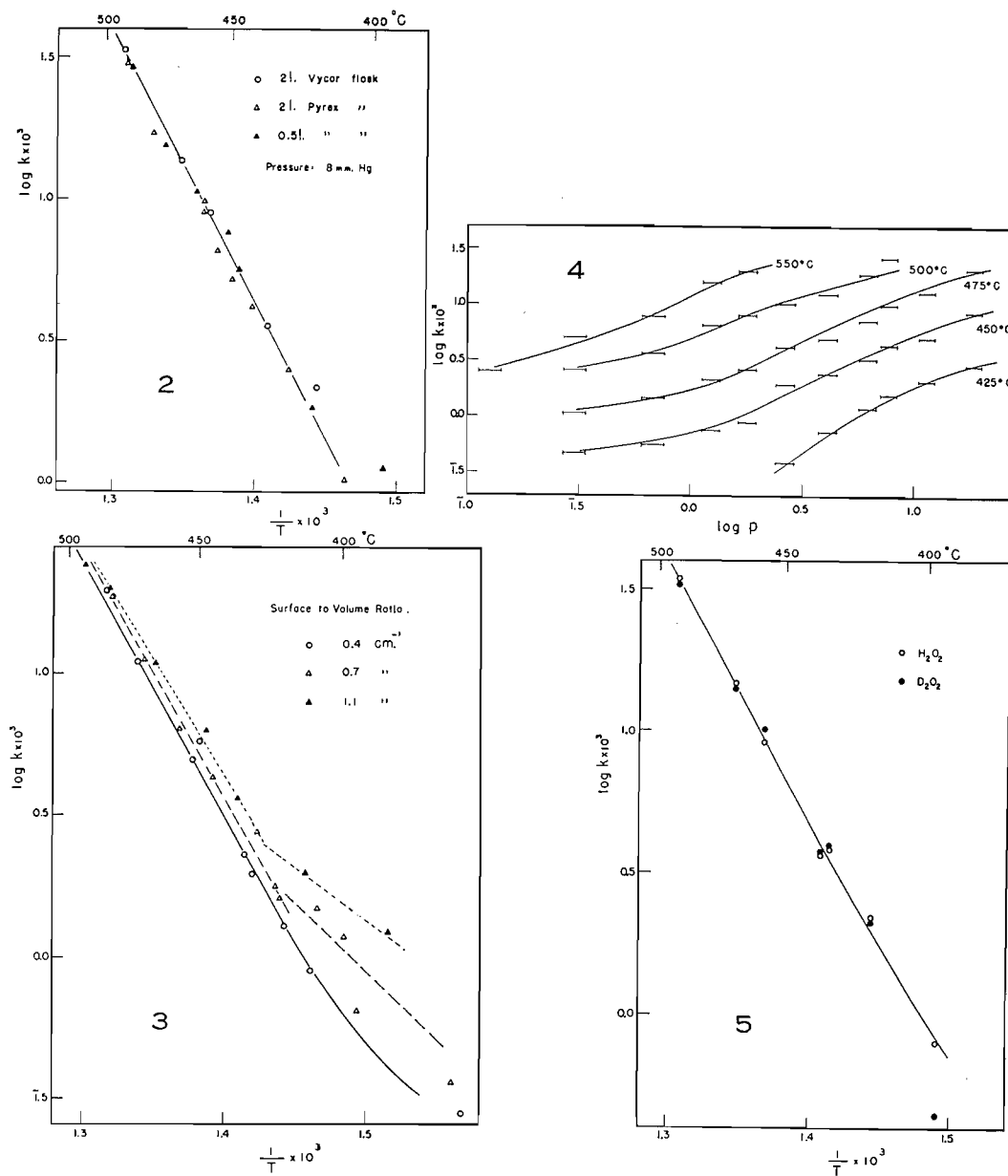


FIG. 2. Rates of decomposition of hydrogen peroxide vapor in different vessels.

FIG. 3. Effect of packing the vessels on the rate of decomposition of hydrogen peroxide vapor.

FIG. 4. Variation with pressure of the rate constant for the decomposition of hydrogen peroxide vapor.

FIG. 5. Compared rate constants for the vapor phase decomposition of hydrogen and deuterium peroxide.

actions, had no more effect on the reaction than the other gases reported above, at least in low concentrations (below 3%). Higher concentrations resulted in side reactions which were not investigated further. Hydrogen, in suitable quantities, led to mild explosions (second limit) but only after nearly all the hydrogen peroxide had decomposed. This interesting phenomenon is being studied in detail and will be described elsewhere. Under

TABLE I
EFFECT OF ADDED GASES ON THE RATE OF DECOMPOSITION OF HYDROGEN PEROXIDE VAPOR

Temp., °C.	Added gas	p_0 , mm.Hg	$p(\text{added gas})/p_0$	$t_{1/2}$, sec.
440	—	7	0	5.8
"	Air	7	0.13	5.8
"	"	7	0.50	5.8
"	"	11	0.32	7.1
"	Hydrogen	8	0.50	5.9
443	—	7	0	6.6
"	Argon	8	0.13	6.9
"	"	13	0.54	7.1
448	—	8	0	7.3
"	Oxygen	8	0.14	7.3
"	"	12	0.45	7.7
451	—	12	0	11
"	Air	12	0.1	11
"	Hydrogen	12	0.09	11
"	Helium	12	0.41	11
445	—	5	0	198
"	Propylene	5	0.05	174
467	—	7	0	78
"	Propylene	7	0.05	78
"	"	7	0.18	72
425	—	7	0	130
"	Nitric oxide	7	0.02	128
447	—	7	0	76
"	Nitric oxide	7	0.04	70
475	—	5	0	33
"	Nitric oxide	5	0.03	35
"	—	7	0	23
"	Nitric oxide	7	0.04	18

otherwise comparable conditions the vapor from more dilute hydrogen peroxide (90%) as well as that from the isotopic peroxide D_2O_2 (95%) was found to decompose at the same rate as the 99.9% material generally used (Fig. 5).

Coatings of fused salts were also tried as they have been claimed to be much more inactive than glass or quartz towards the decomposition of hydrogen peroxide (15). However, they were found unsuitable for measurements in a static system. Fused boric acid turned out to be very hygroscopic, the pressure of peroxide (or water) vapor decreasing quickly with time instead of increasing. Borax, even after it was fired at about 750° C., produced very fast, and approximately zero-order decomposition, resulting, no doubt, from diffusion to and from some active spots.

DISCUSSION

The Mechanism

The above results may be explained satisfactorily, if not uniquely, in terms of the following mechanism for the homogeneous decomposition:



This sequence of elementary reactions involving no chains adds up to the over-all process



We intend to show hereafter that other possible steps are either ruled out or less probable than the above for various reasons. Obviously, mere observations of pressure changes in the system are not sufficient for that purpose and we must rely strongly on evidence from other sources such as spectroscopy, mass spectrometry, electrical discharge work, etc.

It is now well established that the first act in the homogeneous decomposition of hydrogen peroxide is the fission of the O—O bond [1] following activation, thermal or otherwise. Ample evidence for this is provided by the high concentrations of OH radicals found spectroscopically in hydrogen peroxide vapor dissociated by ultraviolet light (28), in the flash photolysis (16) or in an electrical discharge (7). Recent attempts at pyrolysis with the toluene carrier technique have yielded sizable quantities of phenol (23). It must be mentioned, however, that in the *catalyzed* decomposition, no *free* hydroxyls seem to be present. This is indicated by the recent demonstration of Stone and Taylor (25) that carbon monoxide does not react with hydrogen peroxide vapor decomposing heterogeneously at about 110° C., whereas upon irradiation with actinic light the reaction



occurs immediately.

The other conceivable initial step



may be excluded on the grounds that (a) the O—H bond is twice as strong as the O—O bond, and (b) no molecular hydrogen is produced in the reaction. Indeed, it has been proved that both the catalyzed (22) and the photochemical decompositions (29) yield only water and oxygen after equation [5]. As a check we had the non-condensable gas, after complete thermal decomposition, analyzed by mass spectrometry. A sample from hydrogen peroxide decomposition at 470° C. showed 0.1% hydrogen, very near to the limit of detection of that method (0.08%), whereas a sample from deuterium peroxide showed no trace whatsoever of deuterium gas. Therefore, formation of free hydrogen atoms at any stage of the reaction is extremely improbable. Otherwise measurable amounts of hydrogen would appear in the final products as the results of secondary reactions such as:



and even



Incidentally, the formation of free oxygen atoms in the homogeneous decomposition seems just as unlikely as that of hydrogen atoms. The reaction



sometimes postulated is certainly too complex for a single act in the gas phase. Similarly the reaction



suggested by Weiss (30) involves, like reaction [10], a forbidden transition from a singlet to a triplet electronic state. Accordingly, no O⁺ ions have been found in the electron impact dissociation of hydrogen peroxide in a mass spectrometer although the conditions for their detection were very favorable (18).

The most probable step following the initial one is the attack of the parent compound by OH radicals [2], which must be extremely fast. This was confirmed recently by the mass

spectrometric investigations of Foner and Hudson (6) where the highest concentrations of HO_2 radicals were achieved by reacting OH radicals—from dissociated water or hydrogen peroxide vapor—with hydrogen peroxide at low pressures. Also in agreement is the spectroscopic observation that OH radicals disappear much more rapidly in dissociated peroxide vapor than in water vapor (7). Recombination of hydroxyl radicals



need not be considered here since in a non-chain mechanism it results in no over-all reaction. At any rate the probability of such three-body collisions in the gas phase is negligible considering the very low steady-state concentration of OH radicals in the presence of hydrogen peroxide [2].

As for the chain-propagating step



first proposed by Haber and Willstätter (12), it must have an appreciable activation energy, because of its complexity, making it less probable than various termination steps in the gas-phase reaction. As shown below, the present results, as well as those for the photochemical decomposition (29), do not require a chain mechanism. Rather they disprove any appreciable contribution from chains. True, under certain conditions the decomposition of hydrogen peroxide becomes explosive. However, Satterfield and his co-workers (20, 21) have shown that these explosions must be of the thermal type since they usually require a high local temperature: ignition by a spark, by a heated filament, or by fast catalytic decomposition on some very active spot. From extrapolation of their data it would appear that in the high-pressure range of our measurements we were operating within the ignition limits of hydrogen peroxide vapor. Finally it may be recalled here that in the much studied reaction between hydrogen and oxygen, HO_2 radicals are always considered as leading to chain termination rather than propagation (14).

Of the various conceivable termination steps, the most likely are certainly the dismutation reactions [3] and [4]. Again the latter appears by far the less probable of the two, at least until the last stages of the decomposition, owing to the exceedingly strong competition of step [2] for OH radicals.

The Rate Equation

Because of its relatively high activation energy the first step [1] must be rate-determining. Consequently, if the decomposition were a truly elementary process its activation energy should be approximately equal to the bond dissociation energy $D(\text{HO—OH})$, on the very plausible assumption that the reverse reaction requires no activation energy. So far this quantity was taken as 51 kcal. (9) from pertinent thermochemical data and using the generally accepted value $D(\text{O—H}) = 100.2$ kcal. based on the equilibrium measurements of Dwyer and Oldenberg (4). However, this numerical value was admittedly not beyond doubt and it was hoped that the measurements could be repeated with more accuracy (17). Later on they were shown to be open to some criticism (5); an assumed linear relationship between absorption intensity and concentration of OH would tend to make the above value a lower limit. Very recently Barrow and Downie (1) have reported an accurate spectroscopic determination involving only a short Birge-Sponer extrapolation and leading to a slightly higher value of $D(\text{O—H})$, 101.4 ± 0.5 kcal. This is considered the most reliable to date (13) and we will adopt it for the present

discussion. Consequently the value of $D(\text{HO}-\text{OH})$ is found to be 48.5 kcal. from accepted heats of reaction reduced to 0° K. (9, 19).

Now the present reaction rates measured at initial pressures of about 10 mm. Hg and at temperatures above 400° C. may be fitted fairly closely to the equation

$$k = 10^{10.7} \exp(-42,500/RT) \text{ sec.}^{-1}$$

A discrepancy of 6 kcal. is certainly beyond the estimated uncertainty of our experimental activation energy. On further analysis of the results, however, we reflected that the observed rate constants, k_e , were the sum of two terms: k_g for the gas-phase reaction and k_s for the residual surface reaction. The experimental rates should, therefore, be corrected for the latter, a fairly important correction particularly in the transition range, 400°–430° C. To that end the low-temperature portion of the Arrhenius curve extending down to about 300° (Fig. 3) was extrapolated as accurately as possible into the region of homogeneous decomposition and the approximate k_s thus obtained were subtracted from the measured k_e above 400° C. Because of the mutual interference of the two

TABLE II
REACTION RATE CONSTANTS CORRECTED FOR THE RESIDUAL SURFACE
DECOMPOSITION IN 2-LITER FLASKS

Temp., °C.	k_e	k_g	k_g/k_e
A. Acid treated Pyrex flask			
396	1.07	0.661	61.8
431	6.22	5.73	92.1
437	6.46	5.84	90.4
450	11.1	10.4	93.7
454	11.6	10.9	94.0
458	9.82	9.06	92.3
470	23.1	22.3	96.5
471	29.6	28.7	96.9
491	57.8	56.8	98.3
Average E_{act}	44.5 kcal.	48.1 kcal.	
B. Flask A after fusing			
401	1.11	0.681	61.3
402	1.50	1.06	70.7
411	5.78	5.30	91.7
428	4.34	3.77	86.9
430	3.99	3.41	85.5
433	4.52	3.92	86.7
456	13.0	12.3	94.6
456	13.8	13.1	94.9
467	20.0	19.2	96.0
471	26.4	25.5	96.7
482	46.2	45.3	98.1
488	53.3	52.3	98.1
Average E_{act}	44.5 kcal.	48.1 kcal.	
C. Peroxide treated Vycor flask			
384	0.315		
397	0.520	1.107	20.6
410	1.61	1.14	70.8
412	0.82	0.334	40.7
429	3.74	3.16	84.5
442	5.72	5.04	89.1
449	7.85	7.15	91.1
455	10.0	9.26	92.6
460	11.0	10.2	92.7
480	25.3	24.1	95.3
Average E_{act}	43.0 kcal.	48.4 kcal.	

decomposition processes this correction yields only a first approximation. However, no significant improvement was obtained after iteration. The recalculated rate constants for three different reaction vessels are given in Table II, from which it is seen that the average activation energy for the homogeneous process alone, $E = 48 \pm 3$ kcal., agrees well with the above value of $D(\text{HO}-\text{OH})$. The graph in Fig. 6 shows that in our experi-

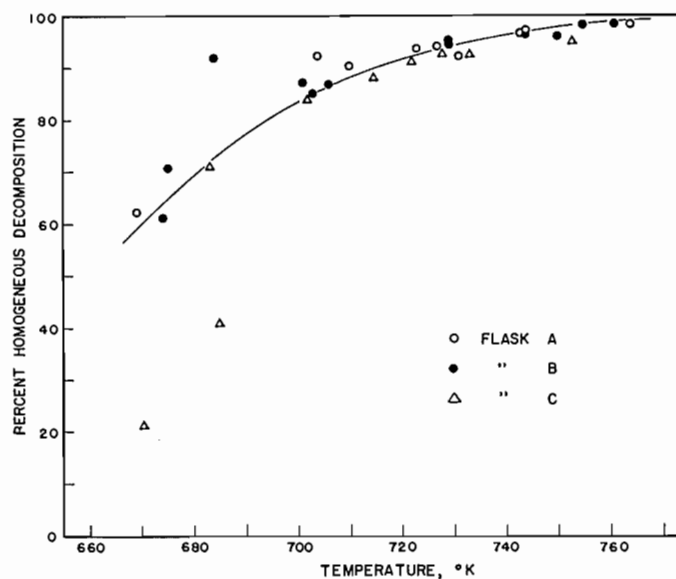


FIG. 6. Fraction of hydrogen peroxide vapor decomposing homogeneously at various temperatures in 2-liter flasks.

ments the decomposition was homogeneous to the extent of about 60% at 400° C. and 90% at 450° C. in 2-liter vessels. Obviously the uncertainty here is greater than for the original data. The results for the decomposition of deuterium peroxide were not numerous enough for similar calculations; at any rate expected difference between the dissociation energy of the two isotopic molecules (about 1 kcal.) is well within the accuracy of our measurements.

In the above reasoning a number of minor points have been overlooked, such as the following two, for instance: (a) The transition state theory of unimolecular reactions (26) predicts that the observed activation energy will be greater than the corresponding bond energy by RT , i.e. some 1.5 kcal. in our case. (b) The decomposition of gaseous hydrogen peroxide is exothermic by about 26 kcal. at 400°–500° C. Now, assuming that convection is unimportant, the mean time for establishment of stationary states in peroxide vapor is found to be of the order of half a minute in a 500 ml. flask and 1 minute in a 2-liter flask. Therefore, the self-heating effect becomes appreciable in the higher temperature and pressure ranges, as may be judged from the figures in Table III calculated by the method of Benson (3). This effect, like the previous one, is still within the estimated accuracy of the calculated activation energy.

Substitution of the corrected activation energy 48 kcal. in the Arrhenius equation leads to a frequency factor A near the expected value for a unimolecular reaction 10^{13} .

We are inclined to consider the excellent agreement of our recalculated results with the predictions of the theory as a confirmation that the homogeneous decomposition of

TABLE III
 TEMPERATURE GRADIENTS IN THE DECOMPOSITION OF HYDROGEN PEROXIDE VAPOR

Size of vessel	Initial pressure, mm. Hg					
	5		10		15	
	Temperature, ° C.					
	430°	480°	430°	480°	430°	480°
500 ml.	0.25°	1.4°	0.68°	4.3°	1.1°	6.6°
2 liters	0.64°	3.6°	1.7°	11°	2.7°	17°

hydrogen peroxide vapor proceeds mainly, if not exclusively, through initial splitting into OH radicals followed by fast, non-chain reactions. Any appreciable contribution from chains would imply higher rates than those observed. In point of fact this constitutes stronger evidence against a chain mechanism than the few tests mentioned above. Thus the negative effect from a threefold increase of the surface-to-volume ratio (Fig. 3) could be explained if chains were initiated *and* broken on the surface. Likewise, the failure of such standard chain inhibitors as nitric oxide and propylene (Table I) is of no definite significance here because so little is known of the reactions of these molecules with hydrogen peroxide.

According to the theory of simple unimolecular reactions (27) the specific reaction rate at a given temperature approaches a constant value k_{∞} at a certain limiting value of the concentration or pressure, as shown in Fig. 5. (As explained before these curves do not fall off steadily at lower pressures because of increasing relative importance of the surface reaction.) Now a rough estimate of this upper-limit pressure may be made from the relationship derived by Benson (2) between the average rate of decomposition $\bar{k}(\epsilon)$ and the normal vibration frequencies of the activated complex ($\bar{\nu}$). Using for the latter some plausible averages, around 1000 cm^{-1} as in most bond-breaking reactions, we find, for the present case, $\bar{k}(\epsilon) = 3.1 \times 10^8 \text{ sec}^{-1}$ at 475°C . The collision frequency z^0 at that temperature being $3 \times 10^{-10} \text{ sec}^{-1}$ and the number of molecules per unit volume $N^0 = 1.3 \times 10^{16} \times p$, the limiting pressure is found to be

$$p = 3 \times 10^8 / 1.3 \times 10^{16} \times 3.1 \times 10^{-10} = 75 \text{ mm. Hg.}$$

A short extrapolation of the curves in Fig. 4 confirms that this result is roughly of the right order of magnitude. Because of the experimental difficulties involved we have not yet succeeded in checking that point.

In conclusion the above results emphasize the futility of attempting to measure the purely homogeneous decomposition of hydrogen peroxide at ordinary temperature. From the rate equation for the thermal reaction it is clear that in the complete absence of catalysts and high-energy radiation hydrogen peroxide would be indefinitely stable at moderate temperatures (average life of the order of 10^7 years at 100°C .).

RÉSUMÉ

On a mesuré la vitesse de décomposition du peroxyde d'hydrogène à l'état gazeux dans un système statique sous des pressions allant de 0.2 à 20 mm. de mercure et dans l'intervalle de température entre 300° et 600°C . La réaction était toujours du premier ordre et les seuls produits étaient la vapeur d'eau et l'oxygène. Au-dessus de 400°C . et

dans des récipients de verre soigneusement nettoyés la réaction homogène l'emportait sur la réaction de surface, et l'énergie d'activation passait brusquement de 10 ou 12 kcal. à environ 43 kcal. En corrigeant les résultats expérimentaux pour la décomposition catalytique on arrive à l'expression

$$k = 10^{13} \exp(-48000/RT) \text{ sec.}^{-1}$$

pour la réaction homogène entre 400° et 500° C. et sous des pressions supérieures à 10 mm. L'énergie d'activation ainsi obtenue est à peu près égale à l'énergie de dissociation de la liaison O—O. Le peroxyde de deutérium se décompose à la même vitesse que le peroxyde d'hydrogène dans les mêmes conditions. Les résultats peuvent s'expliquer adéquatement par une suite de réactions élémentaires, sans chaînes.

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REFERENCES

1. BARROW, R. F. and DOWNIE, A. R. *Proc. Phys. Soc. A*, **69**, 178 (1956).
2. BENSON, S. W. *J. Chem. Phys.* **20**, 1064 (1952).
3. BENSON, S. W. *J. Chem. Phys.* **22**, 46 (1954).
4. DWYER, R. J. and OLDENBERG, O. *J. Chem. Phys.* **12**, 351 (1944).
5. EDSE, R. Third Symposium on Combustion Flame and Explosion Phenomena. Williams & Wilkins Co., Baltimore. 1949. Paper No. 79, p. 611.
6. FONER, S. N. and HUDSON, R. L. *J. Chem. Phys.* **23**, 1364 (1955).
7. FROST, A. A. and OLDENBERG, O. *J. Chem. Phys.* **4**, 781 (1935).
8. GIGUÈRE, P. A. *Can. J. Research, B*, **25**, 135 (1947).
9. GIGUÈRE, P. A. and LIU, I. D. *J. Am. Chem. Soc.* **77**, 6477 (1955).
10. GIGUÈRE, P. A. and LIU, I. D. *Can. J. Technol.* **34**, 473 (1957).
11. GIGUÈRE, P. A., SECCO, E. A., and EATON, R. S. *Discussions Faraday Soc.* **14**, 104 (1953).
12. HABER, F. and WILLSTATTER, R. *Ber.* **64**, 2844 (1931).
13. HERZBERG, G. Private communication.
14. LEWIS, B. and VON ELBE, G. *Combustion, flames and explosions of gases*. Academic Press, Inc., New York. 1951.
15. McLANE, C. K. *J. Chem. Phys.* **17**, 379 (1949).
16. NORMAN, I. and PORTER, G. *Proc. Roy. Soc. A*, **230**, 399 (1955).
17. OLDENBERG, O. *J. Chem. Phys.* **17**, 1059 (1949).
18. ROBERTSON, A. J. B. *Trans. Faraday Soc.* **48**, 228 (1952).
19. ROSSINI, F. D. Selected values of thermodynamic properties. Natl. Bur. Standards (U.S.) Circ. 500. 1952.
20. SATTERFIELD, C. N., CECCOTTI, P. J., and FELDBRUGE, A. H. R. *Ind. Eng. Chem.* **47**, 1040 (1955).
21. SATTERFIELD, C. N., KAVANAGH, G. M., and RESNICK, H. *Ind. Eng. Chem.* **43**, 2507 (1951).
22. SCHUMB, W. C., SATTERFIELD, C. N., and WENTWORTH, R. L. *Hydrogen peroxide*. Reinhold Publishing Corp., New York. 1955.
23. SEHON, A. Private communication.
24. STEIN, T. W. Unpublished results. Quoted in Ref. 22.
25. STONE, F. S. and TAYLOR, H. S. *J. Chem. Phys.* **20**, 1339 (1952).
26. SZWARC, M. *Chem. Revs.* **47**, 75 (1950).
27. TROTMAN-DICKENSON, A. F. *Gas kinetics*. Butterworths, London. 1955.
28. UREY, H. C., DAWSEY, L. H., and RICE, F. O. *J. Am. Chem. Soc.* **51**, 137 (1929).
29. VOLMAN, D. H. *J. Chem. Phys.* **17**, 947 (1949).
30. WEISS, J. *Trans. Faraday Soc.* **36**, 856 (1940).

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1. Hanna Kierzkowska-Pawlak, Jacek Tyczkowski, Arkadiusz Jarota, Halina Abramczyk. 2019. Hydrogen production in liquid water by femtosecond laser-induced plasma. *Applied Energy* **247**, 24-31. [[Crossref](#)]
2. Kaikai Kou, Wei Zhou, Yan Wang, Haiqian Zhao, Jihui Gao. 2019. Investigation of Advanced NO Oxidation Process with the Delivery of $\cdot\text{OH}$ from Thermal Decomposition of H_2O_2 . *The Canadian Journal of Chemical Engineering*. [[Crossref](#)]
3. Takao Tsuneda, Junpei Miyake, Kenji Miyatake. 2018. Mechanism of H_2O_2 Decomposition by Triphenylphosphine Oxide. *ACS Omega* **3**:1, 259-265. [[Crossref](#)]
4. Takao Tsuneda, Tetsuya Taketsugu. 2018. Theoretical investigations on hydrogen peroxide decomposition in aquo. *Physical Chemistry Chemical Physics* **20**:38, 24992-24999. [[Crossref](#)]
5. Zaid B. Jildeh, Patrick Kirchner, Jan Oberländer, Alexander Kremers, Torsten Wagner, Patrick H. Wagner, Michael J. Schöning. 2017. FEM-based modeling of a calorimetric gas sensor for hydrogen peroxide monitoring. *physica status solidi (a)* **214**:9, 1600912. [[Crossref](#)]
6. Noha A. El Essawy, Abdelaziz H. Konsowa, Mohamed Elnouby, Hassan A. Farag. 2017. A novel one-step synthesis for carbon-based nanomaterials from polyethylene terephthalate (PET) bottles waste. *Journal of the Air & Waste Management Association* **67**:3, 358-370. [[Crossref](#)]
7. Mindaugas Jonusas, Lahouari Krim. 2016. A possible answer to the mysterious non-detection of hydroxylamine in space: the thermal desorption mechanism. *Monthly Notices of the Royal Astronomical Society* **459**:2, 1977-1984. [[Crossref](#)]
8. Jan Oberländer, Zaid Jildeh, Patrick Kirchner, Luisa Wendeler, Alexander Bromm, Heiko Iken, Patrick Wagner, Michael Keusgen, Michael Schöning. 2015. Study of Interdigitated Electrode Arrays Using Experiments and Finite Element Models for the Evaluation of Sterilization Processes. *Sensors* **15**:10, 26115-26127. [[Crossref](#)]
9. Graeme Moad, Ian J. Dagley, Jana Habsuda, Christopher J. Garvey, Guoxin Li, Lance Nichols, George P. Simon, Maria Rossella Nobile. 2015. Aqueous hydrogen peroxide-induced degradation of polyolefins: A greener process for controlled-rheology polypropylene. *Polymer Degradation and Stability* **117**, 97-108. [[Crossref](#)]
10. Jan Oberländer, Alexander Bromm, Luisa Wendeler, Heiko Iken, Marlena Palomar Durán, Anton Greeff, Patrick Kirchner, Michael Keusgen, Michael Josef Schöning. 2015. Towards a biosensor to monitor the sterilisation efficiency of aseptic filling machines. *physica status solidi (a)* **212**:6, 1299-1305. [[Crossref](#)]
11. Roghaye Nurazar, Zahra Fallah Ebrahimi, Mehdi D. Esrafil, Esmail Vessally. 2015. Sensing and catalytic decomposition of hydrogen peroxide by silicon carbide nanotubes: A DFT study. *International Journal of Quantum Chemistry* **115**:8, 471-476. [[Crossref](#)]
12. Stefano Scaramuzza, Stefano Agnoli, Vincenzo Amendola. 2015. Metastable alloy nanoparticles, metal-oxide nanocrescents and nanoshells generated by laser ablation in liquid solution: influence of the chemical environment on structure and composition. *Physical Chemistry Chemical Physics* **17**:42, 28076-28087. [[Crossref](#)]
13. Mahdi Ghelichi, Pierre-Éric Alix Melchy, Michael H. Eikerling. 2014. Radically Coarse-Grained Approach to the Modeling of Chemical Degradation in Fuel Cell Ionomers. *The Journal of Physical Chemistry B* **118**:38, 11375-11386. [[Crossref](#)]
14. Vadim V. Krongauz, John F. O'Connell, Michael T. K. Ling. 2014. Kinetics of catalyst-free thermal and photo-oxidation of cumene. *Journal of Thermal Analysis and Calorimetry* **116**:3, 1285-1299. [[Crossref](#)]
15. Jan Oberländer, Patrick Kirchner, Hans-Gerd Boyen, Michael J. Schöning. 2014. Detection of hydrogen peroxide vapor by use of manganese(IV) oxide as catalyst for calorimetric gas sensors. *physica status solidi (a)* **211**:6, 1372-1376. [[Crossref](#)]
16. Miao Yang, Mats Jonsson. 2014. Evaluation of the O_2 and pH Effects on Probes for Surface Bound Hydroxyl Radicals. *The Journal of Physical Chemistry C* **118**:15, 7971-7979. [[Crossref](#)]
17. Dulce M. Perez Ferrandez, Mart H. J. M. de Croon, Jaap C. Schouten, T. Alexander Nijhuis. 2013. Gas-Phase Epoxidation of Propene with Hydrogen Peroxide Vapor. *Industrial & Engineering Chemistry Research* **130722124305000**. [[Crossref](#)]
18. T. Grewer, L. Küchler, H. Zeininger, K. Hauffe. Reaktionsgeschwindigkeiten 247-359. [[Crossref](#)]
19. J. Troe. 2011. The thermal dissociation/recombination reaction of hydrogen peroxide $\text{H}_2\text{O}_2(+\text{M}) \rightleftharpoons 2\text{OH}(+\text{M})$ III. *Combustion and Flame* **158**:4, 594-601. [[Crossref](#)]
20. John A. Wilson, Raj Pathania, Samson Hettiarachchi. 2009. Environmental controls for higher temperature direct-cycle light water reactors. *Journal of Nuclear Materials* **392**:2, 230-234. [[Crossref](#)]
21. J. Troe, V. G. Ushakov. 2008. SACM/CT Study of the dissociation/recombination dynamics of hydrogen peroxide on an ab initio potential energy surface : Part II. Specific rate constants $k(\text{E}, \text{J})$, thermal rate constants $k_\infty(\text{T})$, and lifetime distributions. *Physical Chemistry Chemical Physics* **10**:26, 3915. [[Crossref](#)]

22. J. H. Corpening, S D. Heister, W. E. Anderson, B. L. Austin. 2006. Thermal Decomposition of Hydrogen Peroxide, Part 2: Modeling Studies. *Journal of Propulsion and Power* **22**:5, 996-1005. [[Crossref](#)]
23. Jong Soo Mok, W Jason Helms, James C. Sisco, William E. Anderson. 2005. Thermal Decomposition of Hydrogen Peroxide, Part I: Experimental Results. *Journal of Propulsion and Power* **21**:5, 942-953. [[Crossref](#)]
24. Nick Pearson, Chris Kachel, William Anderson. Vaporization and Decomposition of Hydrogen Peroxide Drops . [[Crossref](#)]
25. J. S. Mok, J. Sisco, W. Anderson. Analysis and Experiments of Hydrogen Peroxide Vaporization and Decomposition . [[Crossref](#)]
26. Juhani Kronholm, Sami Huhtala, Heikki Haario, Marja-Liisa Riekkola. 2002. Oxidation of 4-chloro-3-methylphenol in pressurized hot water in liquid and vapor phases. *Advances in Environmental Research* **6**:3, 199-206. [[Crossref](#)]
27. Michelle M. Collins, C. David Cooper, John D. Dietz, Christian A. Clausen III, Loubna M. Tazi. 2001. Pilot-Scale Evaluation of H₂O₂ Injection to Control NO_x Emissions. *Journal of Environmental Engineering* **127**:4, 329-336. [[Crossref](#)]
28. F Javier Rivas, Stan T Kolaczowski, Fernando J Beltran, David B McLurgh. 1999. Hydrogen peroxide promoted wet air oxidation of phenol: influence of operating conditions and homogeneous metal catalysts. *Journal of Chemical Technology & Biotechnology* **74**:5, 390-398. [[Crossref](#)]
29. F Javier Rivas, Stan T Kolaczowski, Fernando J Beltran, David B McLurgh. 1999. Hydrogen peroxide promoted wet air oxidation of phenol: influence of operating conditions and homogeneous metal catalysts. *Journal of Chemical Technology & Biotechnology* **74**:5, 390-398. [[Crossref](#)]
30. F Javier Rivas, Stan T Kolaczowski, Fernando J Beltran, David B McLurgh. 1999. Hydrogen peroxide promoted wet air oxidation of phenol: influence of operating conditions and homogeneous metal catalysts. *Journal of Chemical Technology & Biotechnology* **74**:5, 390-398. [[Crossref](#)]
31. F Javier Rivas, Stan T Kolaczowski, Fernando J Beltran, David B McLurgh. 1999. Hydrogen peroxide promoted wet air oxidation of phenol: influence of operating conditions and homogeneous metal catalysts. *Journal of Chemical Technology & Biotechnology* **74**:5, 390-398. [[Crossref](#)]
32. Chaoyang Li, D.R. Olander. 1999. Steam radiolysis by alpha-particle irradiation. *Radiation Physics and Chemistry* **54**:4, 361-371. [[Crossref](#)]
33. F.J. Rivas, S.T. Kolaczowski, F.J. Beltrán, D.B. McLurgh. 1998. Development of a model for the wet air oxidation of phenol based on a free radical mechanism. *Chemical Engineering Science* **53**:14, 2575-2586. [[Crossref](#)]
34. R. Zils, D. Perrin, R. Martin. 1998. Kinetic study and modeling of the hetero-homo-geneous pyrolysis and oxidation of isobutane around 800 K. Part III. Pyrolysis-oxidation in unpacked and in pbO-coated packed Pyrex reactors. *International Journal of Chemical Kinetics* **30**:9, 657-671. [[Crossref](#)]
35. R. Zils, D. Perrin, R. Martin. 1998. Kinetic study and modeling of the hetero-homo-geneous pyrolysis and oxidation of isobutane around 800 K. Part III. Pyrolysis-oxidation in unpacked and in pbO-coated packed Pyrex reactors. *International Journal of Chemical Kinetics* **30**:9, 657-671. [[Crossref](#)]
36. Daojie Dong, George F. Vandegrift. 1997. Alkaline Peroxide Processing of Low-Enriched Uranium Targets for 99 Mo Production —Decomposition of Hydrogen Peroxide. *Nuclear Science and Engineering* **126**:2, 213-223. [[Crossref](#)]
37. C. C. Lin, F. R. Smith, N. Ichikawa, T. Baba, M. Itow. 1991. Decomposition of hydrogen peroxide in aqueous solutions at elevated temperatures. *International Journal of Chemical Kinetics* **23**:11, 971-987. [[Crossref](#)]
38. C. C. Lin, F. R. Smith, N. Ichikawa, T. Baba, M. Itow. 37. Decomposition of hydrogen peroxide in aqueous solutions at elevated temperatures 1: 145-151. [[Crossref](#)]
39. Junichi Takagi, Kenkichi Ishigure. 1985. Thermal Decomposition of Hydrogen Peroxide and Its Effect on Reactor Water Monitoring of Boiling Water Reactors. *Nuclear Science and Engineering* **89**:2, 177-186. [[Crossref](#)]
40. Lilian G. S. Shum, Sidney W. Benson. 1983. Mechanism and thermochemistry of oxidation of HCl and HBr at high temperatures. The heat of formation of HO₂. *International Journal of Chemical Kinetics* **15**:4, 341-380. [[Crossref](#)]
41. Lilian G. S. Shum, Sidney W. Benson. 1983. The oxidation of HI at low temperatures and the heat of formation of HO₂. *International Journal of Chemical Kinetics* **15**:4, 323-339. [[Crossref](#)]
42. Frank K. Truby. 1978. Spontaneous explosions in multiatmosphere H₂-F₂-O₂ mixtures. *Journal of Applied Physics* **49**:6, 3481-3484. [[Crossref](#)]
43. J. Troe, H. Gg. Wagner. Unimolecular Dissociation of Small Molecules 1-80. [[Crossref](#)]
44. K.H. Homann, A. Haas. Chapter 1 Kinetics of the Homogeneous Decomposition of Hydrides 1-45. [[Crossref](#)]
45. A. Tessier, W. Forst. 1971. Kinetics of hydrogen peroxide pyrolysis by molecular-beam mass spectrometry. *International Journal of Mass Spectrometry and Ion Physics* **7**:4, 281-295. [[Crossref](#)]

46. M. Senegačnik, C. Klofutar, Š. Paljk. 1971. The extraction of nitric acid into 1,2-dichloro ethane solution of triphenyl arsineoxide. *Journal of Inorganic and Nuclear Chemistry* **33**:8, 2635-2640. [[Crossref](#)]
47. H. Kijewski, J. Troe. 1971. Study of the pyrolysis of H₂O₂ in the presence of H₂ and CO by use of UV absorption of HO₂. *International Journal of Chemical Kinetics* **3**:3, 223-235. [[Crossref](#)]
48. T. Joseph Varkey, Samuel Sandler. 1969. The low-temperature oxidation of 2-methylbutane in a flow system during the 'induction period'. *Combustion and Flame* **13**:3, 223-236. [[Crossref](#)]
49. E. Meyer, H.A. Olschewski, J. Troe, H.Gg. Wagner. 1969. Investigation of N₂H₄ and H₂O₂ decomposition in low and high pressure shock waves. *Symposium (International) on Combustion* **12**:1, 345-355. [[Crossref](#)]
50. Norisuke H Ata, Paul A. Glguère. 1966. STUDIES ON HYDROGEN-OXYGEN SYSTEMS IN THE ELECTRIC DISCHARGE: I. THE REACTIONS OF HYDROGEN ATOMS WITH HYDROGEN PEROXIDE. *Canadian Journal of Chemistry* **44**:8, 869-876. [[Crossref](#)]
51. R.R. Baldwin, D. Jackson, R.W. Walker, S.J. Webster. 1965. The use of the hydrogen-oxygen reaction in evaluating velocity constants. *Symposium (International) on Combustion* **10**:1, 423-433. [[Crossref](#)]
52. R.R. Baldwin, D. Jackson, R.W. Walker, S.J. Webster, Peter Gray, J.C.J. Thynne, R.V. Blundell, W.G.A. Cook, D.E. Hoare, G.S. Milne. 1965. The use of the hydrogen-oxygen reaction in evaluating velocity constants. *Symposium (International) on Combustion* **10**:1, 423. [[Crossref](#)]
53. F. W. Evans, A. H. Sehon. 1963. THE THERMAL DECOMPOSITION OF PERACETIC ACID IN AROMATIC SOLVENTS. *Canadian Journal of Chemistry* **41**:7, 1826-1831. [[Abstract](#)] [[PDF](#)] [[PDF Plus](#)]
54. J.C. Polanyi. Chemical Processes 807-855. [[Crossref](#)]
55. C.N. Satterfield, E. Kehat. 1961. Burning velocities of the hydrogen peroxide decomposition flame. *Combustion and Flame* **5**, 273-282. [[Crossref](#)]
56. R.R. Baldwin, P. Doran, L. Mayor. 1961. The dissociation of hydrogen peroxide and its role in the hydrogen-oxygen reaction. *Symposium (International) on Combustion* **8**:1, 103-109. [[Crossref](#)]
57. R.R. Baldwin, D. Brattan. 1961. Homogeneous gas-phase decomposition of hydrogen peroxide. *Symposium (International) on Combustion* **8**:1, 110-119. [[Crossref](#)]
58. Z. G. Szabó. Reaktionen einer Art Ausgangsmolekeln 81-152. [[Crossref](#)]
59. P. A. Giguère. 1959. Revised Values of the O-O and the O-H Bond Dissociation Energies. *The Journal of Chemical Physics* **30**:1, 322-322. [[Crossref](#)]
60. W. Forst. 1958. SECOND-ORDER UNIMOLECULAR KINETICS IN THE THERMAL DECOMPOSITION OF HYDROGEN PEROXIDE VAPOR. *Canadian Journal of Chemistry* **36**:9, 1308-1319. [[Crossref](#)]
61. D. E. HOARE, J. B. PROTHEROE, A. D. WALSH. 1958. Thermal Decomposition of Hydrogen Peroxide Vapour. *Nature* **182**:4636, 654-654. [[Crossref](#)]
62. Robert C. Gore. 1958. Infrared Spectroscopy. *Analytical Chemistry* **30**:4, 570-579. [[Crossref](#)]
63. N.S. Enikolopyan, D.J. Waddington, J.S. Watson. 1958. Kinetics and mechanism of methane oxidation. *Symposium (International) on Combustion* **7**:1, 157. [[Crossref](#)]
64. J.S. Watson. 1958. The mercury photosensitized hydrogen-oxygen reaction at low oxygen concentrations. *Symposium (International) on Combustion* **7**:1, 17-22. [[Crossref](#)]